DEVELOPMENT OF A NEW FRACTURING FLUID SYSTEM FOR TIGHT RESERVOIRS

BY

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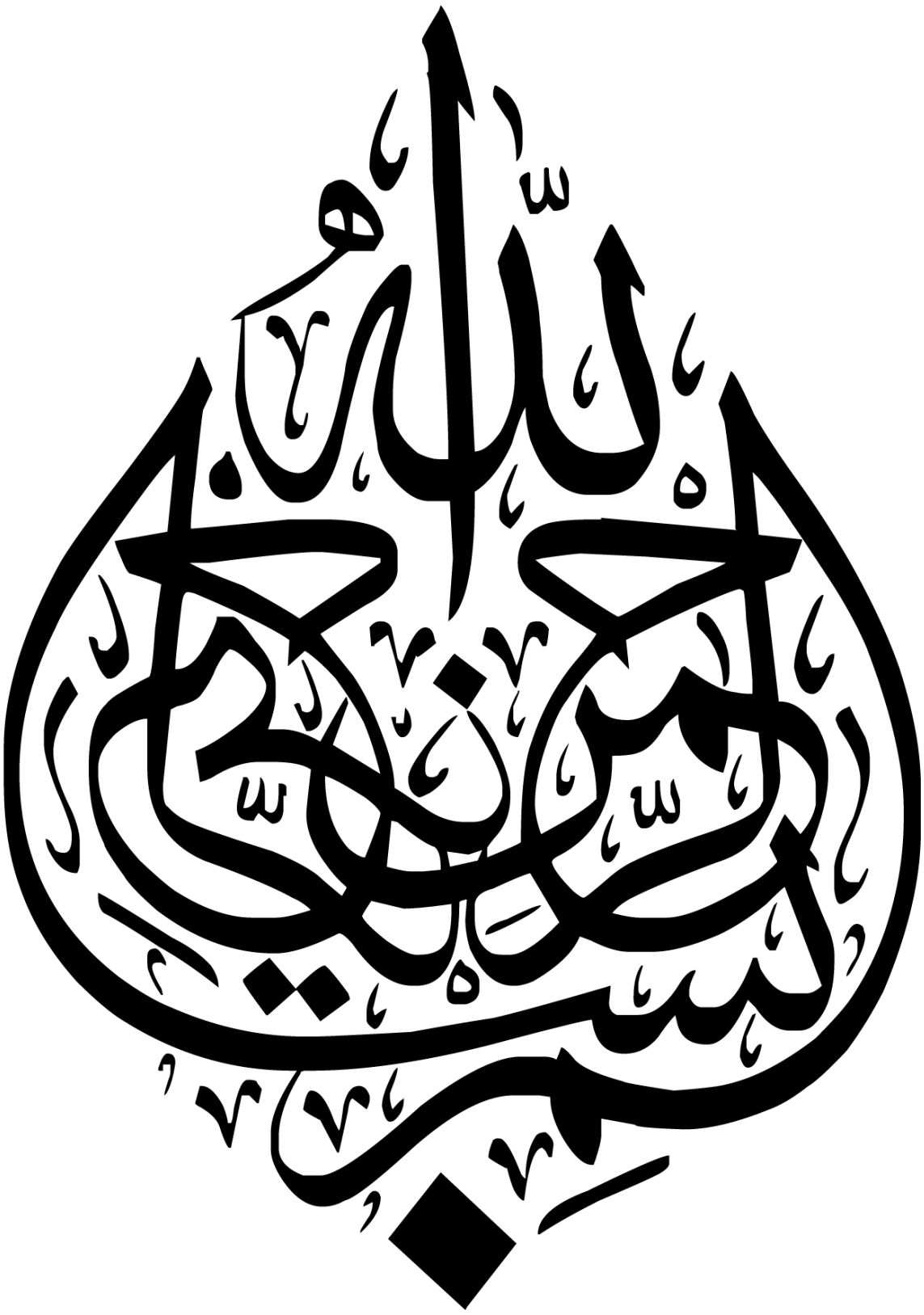

To my beloved Father,

To my precious Mother,

To my Sisters, for ceaselessly being my source of strength,

To my Fiancée, for always pushing me to go to greater lengths,

To my Teachers, To my Friends …

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LIST OF ABBREVIATIONS

APT	:	Aqueous Phase Trapping
CT-Scan	:	Computed Tomography Scan
DI-Water	:	Deionized Water
FTIR	:	Fourier Transform Infrared Spectroscopy
GLDA	:	Glutamic Acid – Diacetic Acid
HF/HA	:	Hydraulic Fracturing/Acid Fracturing
HPAM	:	Hydrolyzed Polyacrylamide
HPG	:	Hydroxypropyl Guar
IFT	:	Interfacial Tension
PPTG	:	Pound per Thousand Gallons (Solids Concentration Unit)
TDS	:	Total Dissolved Solids
TVP	:	Thermoviscosifying Polymer
XC	:	Xanthan Polymer

ABSTRACT

Full Name : Marwan Nagm Eldeen Elnour Mohammed

Thesis Title : Development of a New Fracturing Fluid System for Tight Reservoirs

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Hydraulic Fracturing (Proppant and Acid) are considered one of the most important stimulation methods. Hydraulic Fracturing is carried out by inducing fracture/s in the formation to create conductive pathways for the flow of hydrocarbon. The pathways are kept open either by using proppant or by etching the fracture surface using acids.

A typical fracturing fluid usually consists of a gelling agent (Polymers), cross-linkers, buffers, clay stabilizers, gel stabilizers, biocide, surfactants, and breakers mixed with fresh water. The numerous additives are used to prevent damage resulting from such operations, or better yet, enhancing it beyond just the aim of a fracturing operation.

This study introduces a new smart fracturing fluid system that can be either used for proppant fracturing (high pH) or acid fracturing (low pH) operations in sandstone formations, the fluid system consists of GLDA that has the abilities of a cross-linker, breaker, biocide, clay stabilizer, replacing all the mentioned constituents of a typical fracturing fluid into one simple fluid. GLDA is also a low IFT fluid which will reduce the IFT eliminating the Water-Blockage effect. GLDA is compatible and stable with sea water which is advantageous over the typical fracturing fluid. It is also stable in high temperature reservoirs (up to 300°F) and it is also environmentally friendly and readily

biodegradable. The new fluid system was tested and evaluated in terms of rheology, fluid loss, and filter cake integrity against a low permeability sandstone core sample as well as high permeability one.

The new fracturing fluid formulation can withstand up to 300°F of formation temperature and stable for about six hours under high shearing rates ($511s^{-1}$), the new formulation breaks on its own and the delay time or breaking time can be controlled with the concentrations of the constituents of the fluid (GLDA or polymer).

Coreflooding experiments were conducted using Scioto and Berea sandstone cores to evaluate the effectiveness of the developed fluid. The flooding experiments were in reasonable conformance with the rheological properties of the developed fluid regarding the thickening and breaking time as well as yielding high return permeability.

ملخص الرسالة

الاسم الكامل: مروان نجم الدين النور محمد

عنوان الرسالة: تطوير مائع جديد لعمليات التكسير الهيدروليكي للمكامن ذات النفاذية الضيقة

التخصص: هندسة النفط

تاريخ الدرجة العلمية: يناير٢٠١٧ ميلادي، الموافق ربيع الثاني ١٤٣٩ هجري

التكسير الهيدروليكي (بواسطة الدعامات أو الأحماض) تعتبر واحدة من أساليب تحفيز المكامن النفطية الأكثر أهمية في الأنشطة البترولية في الوقت الحاضر، ويتم ذلك عن طريق إحداث كسر أو عدة كسور في الطبقات المنتجة للبترول لخلق مسارات موصلة لتدفق النفط أوالغاز من خلالها، ويتم الاحتفاظ بالمسارات مفتوحة إما باستخدام الدعامات أو عن طريق الحفر على سطح الكسر (أو الكسور) باستخدام الأحماض. تمثل مكامن البترول ذات النفاذية الضيقة حوالي ٦٠% من الموارد غير التقليدية العالمية، و تحتوي هذه المكامن على كميات كبيرة من النفط والغاز داخلها، ولكن نظرا لضيق النفاذية فيها يعتبر الإنتاج منها غير مجدي اقتصاديا مما يجعل التكسير الهيدروليكي هي التقنية الواعدة للتعامل مع هذه الأنواع من المكامن.

في الوقت الحالي يعتبر التكسير الهيدروليكي محور العديد من الأبحاث في جميع أنحاء العالم للحد من الضرر النسبي الناتج عن هذه العمليات على المكامن البترولية، وقد صنعت عدة موائع لتحقيق ذلك. أحدثها الذي يتألف من البوليمرات، وروابط البوليمرات، ومضادات البكتريا المستهلكه للكبريتات الموجودة في المكامن، ومثبتات الطين، ومثبتات الهلام، ومثبطات التوتر السطحي و قواطع البوليمرات مخلوطة مع المياه العذبة، وكلها لمنع الأضرار الناجمة عن هذه العمليات، أو الأفضل من ذلك، تعزيز الإنتاجية من هذه المكامن بدلا من مجرد كسرها فقط.

هذه الدراسة تقدم نظام جديد لمائع كسر يمكن استخدامه إما للكسر بالدعامات (عند درجة حموضة عالية) أو للكسر بالحمض (عند درجة حموضة منخفضة) للمكامن التي تحتوي على طبقات رملية ذات النفاذية الضيقه، ويتكون المائع من (GLDA أحد السوائل المخلبية) الذي لديه القدرة على ان يحل محل روابط البوليمرات وقواطعها ، ومضادات البكتريا المستهلكه للكبريتات الموجودة في المكامن، ومثبتات الطين ، مستبدلا بذلك معظم مكونات موائع الكسر النمطية المذكورة في مائع واحد بسيط ، (GLDA) أيضا لديه القدرة على تخفيض التوتر السطحي بين الماء و

الطبقات المنتجة ، الأمر الذي سيسهل التخلص من ظاهرة انسداد الطبقات بالماء أو انحباس الماء داخلها. (GLDA) ايضا متوافق ومستقر مع مياه البحر على عكس موائع الكسر النمطية. كما انه مستقر في المكامن ذات درجة حرارة عالية (تصل إلى ٣٠٠ درجة فهرنهايت) غير أنه صديق للبيئة. وقد تم اختبار مائع الكسر الجديد وتقييمه من حيث الريولوجيا، وتسريبه الى داخل الطبقات، وسلامة كعكة المتشكلة منه مع الطبقات ذات النفاذية الضيقة. و تمت دراسة إزالة ظاهرة انسداد الطبقات بالماء وتقييمها.

مائع الكسر الجديد يمكن أن يتحمل ما يصل الى ٢٥٠ درجة فهرنهايت ومستقر لمدة ٦ ساعات تحت معدلات القص عالية (٥١١ مقلوب الثانية)، غير انه يرط البوليمرات ويفصلها من تلقاء نفسه بعد زمن معين و يمكن السيطرة على ذلك مع تغيير تركيزات مكونات المائع. تم ضخ المائع الجديد خلال عينات صخور ذات النفاذيه المنخفضه لمعرفة مدى فعالية المائع مع هذا النوع من الصخور. مائع الكسر الجديد ايضا نجح في إزالة ظاهرة انسداد الطبقات بالماء الذي يحل قضية رئيسية في التعامل مع هذا النوع من الطبقات (ذات النفاذيه الضيقة)، كما تكلفة صناعة هذه الموائع قليله نسبيا و فعالة.

CHAPTER 1

INTRODUCTION

Hydraulic fracturing and acid fracturing operations are currently considered one of the most important activities in oil and gas industry. Hydraulic Fracturing (Figure 1.1 - a & b) is inducing a fracture or multiple fractures in the formation using a fluid that is injected into the formation at high pressure to form high permeability pathways (Slab shaped zones) to stimulate and enhance the producing wells. These fractures are then kept open using a proppant, thus preventing the closure of those fractures due to stresses acting on the formation, on the other hand in acid fracturing (Figure 1.2 - a & b) the acid is spent to create uneven etches (channels) in the rock (fracture face). In acid fracturing, the formation rock must contain minerals that are partially soluble in the acid used to create those etches.

Hydraulic Fracturing is prominent amongst permeability-impaired formations (low permeability reservoirs) (i.e. Shale-Gas and Tight-Gas -less than 0.5 md for oil and 0.01 md for gas). Hydraulic fracturing significantly improves the productivity (producing economical volumes of gas at economical rates) of the wells hence, the overall recovery factor. Hydraulic fracturing is also widely used in moderate permeability reservoirs (up to 50 md for oil and 1 md for gas) with large skin around the vicinity of the wellbore by bypassing the damaged zone to further enhance the flow of hydrocarbon, allowing for accelerated production without impacting the

formation reserves negatively. However, this case relies mostly on the economic feasibility of conducting such operations [1].

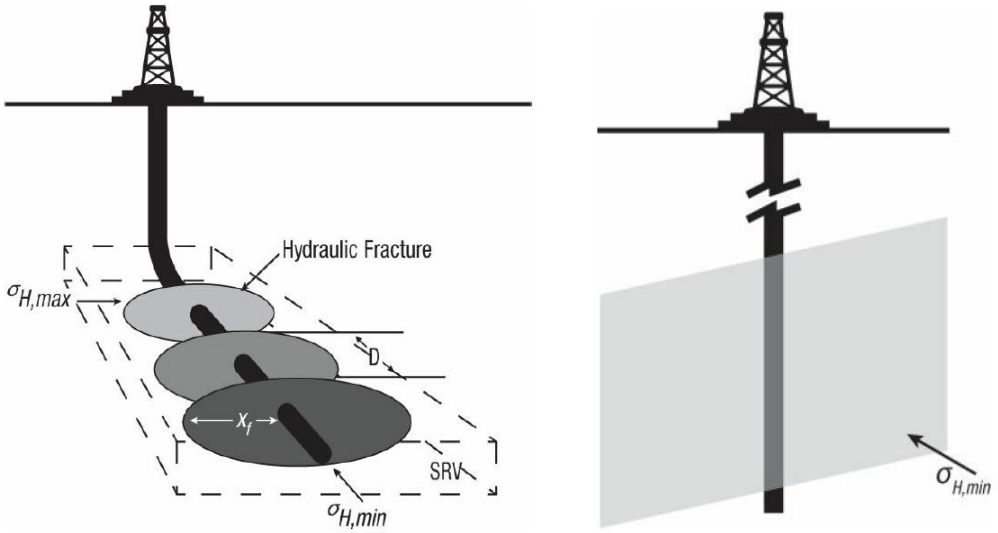

Figure 1.1: Hydraulic Fracturing a) Vertical well, b) Horizontal well

For any successful operation of the hydraulic/acid fracturing, certain important parameters must be taken into consideration. These parameters are; in-situ stresses (fracture closure pressure or minimum compressive stress), formation moduli, permeability, fracture-fluid viscosity, fluid-loss control, pad volume, total volume and rate of fluid injected, and proppant type and amount. The reaction kinetics is also an important factor if acid is to be used, cost. Economic feasibility as well as environmental impacts of hydraulic fracturing are also critical factors. Another important aspect of designing a successful operation is the candidate well chosen for stimulation, selection of the candidate wells depends, as well, on several parameters such as the distribution of in-situ stresses, reservoir depth and pressure, formation temperature reservoir fluid viscosity and the skin factor or the damage near the wellbore.

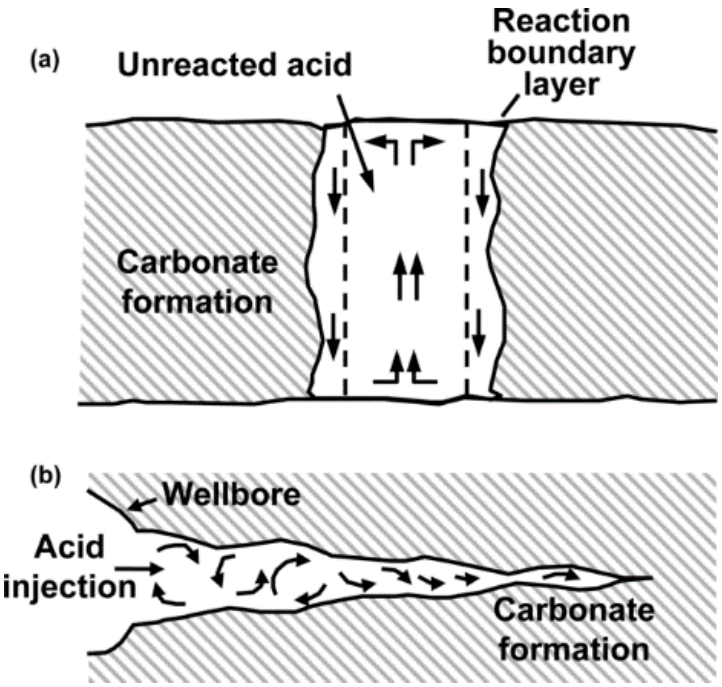

Figure 1.2: Acid Injection

The fracturing fluid must be designed and tested carefully to avoid incompatibility to the formation. Especially if the reservoir contained minerals that are water sensitive such as clay minerals (Smectite, Illite) found in tight gas or shale gas reservoirs, hence causing fines migration, or swelling that results in damaging the reservoir furthermore.

Unconventional resources can be classified into four groups, namely, Shale-Gas, Tight-Gas, Coalbed-Methane and Gas-Hydrates, Tight-Gas reservoirs will be discussed in details, being the scope of this study.

Tight gas reservoirs are responsible for 57 -59% of global unconventional resources (see Figure 1.3). The majority of these reservoirs are in North America, India, China, across Europe and recently countries in the middle east and North Africa [2]. Due to the large quantities of gas in those formations, any enhancement on their recovery is

of great importance. Tight reservoirs are those reservoirs that are characterized by a low permeability (i.e. less than 0.5 mD), they are either carbonate or sandstone reservoirs [2], [3]. Another definition of tight gas reservoirs are sandstone or carbonate reservoirs that are of low permeability and require reservoir stimulation and drilling technology to recover the gas at economic flow rates. This definition is conveniently broad because permeability is not the only contributing parameter defining those formations. Reservoir pressure and temperature, fluid properties, surface temperatures, permeability, drainage, and wellbore radii, pay thickness, skin damage and non-Darcy effect. Natural fractures (if existed) and their distribution, all contribute in the production of gas from tight formations and should not be disregarded [4]. Tight sandstone formations are mostly water-wet, they are all mostly under-saturated reservoirs where gas desorption controls the gas production rather than matrix flow. The low permeability of the tight gas reservoirs is due to the small grain size in sandstones and limited inter-crystalline porosity development in carbonates [3].

Problems associated with tight gas production in drilling or hydraulic fracturing operations include Aqueous Phase Trapping, Natural Fractures (Fluid leak-off), folding and faulting (making the prediction of fracture pressure difficult), and fluid incompatibility with the formation.

Water Blockage or Aqueous Phase Trapping (APT) is a serious problem in tight formations among others, consequently, many fracturing fluids were suggested as a solution to this problem such as: Pure Hydrocarbon (Oil-based fluid), CO_2 energized

Oil-based fluid, cross-linked water-based, water based foam and poly-emulsion. A detailed evaluation of these fluids will be discussed in the literature review chapter.

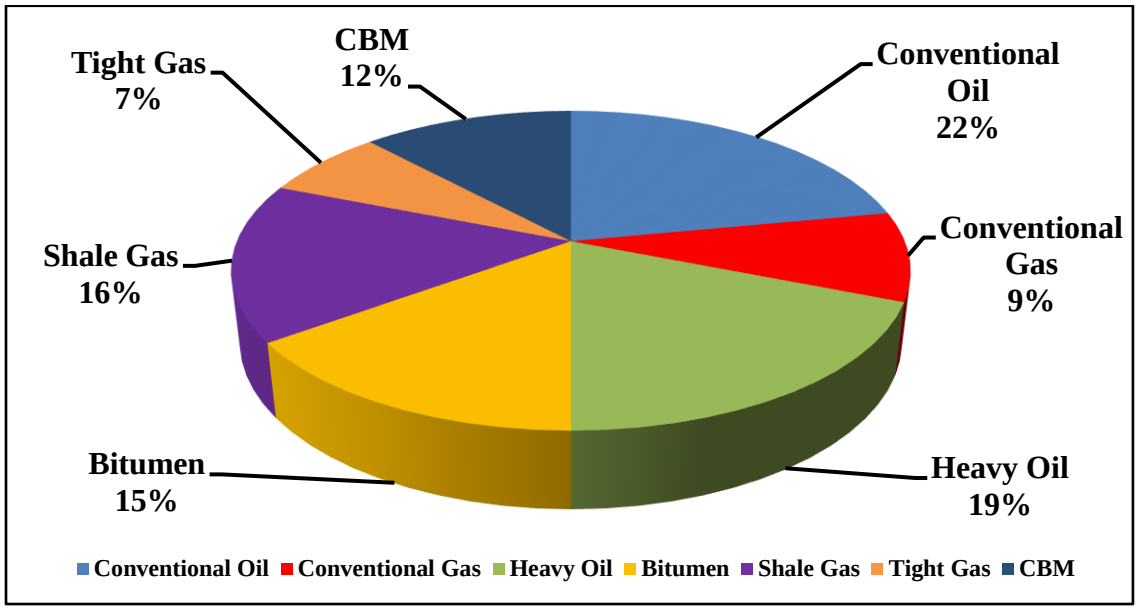

Figure 1.3: World Hydrocarbon Reserves, from "http://www.radialdrilling.com/?page_id=17130"

This study introduces a new smart fracturing fluid system that can be either used for proppant fracturing (high pH) or acid fracturing (low pH) operations in tight as well as conventional formations. The fluid system consists of GLDA that has the abilities of a cross-linker, breaker, biocide, and clay stabilizer replacing all the typical constituents of a fracturing fluid into one simple fluid. GLDA is compatible and stable with both fresh water and seawater which is advantageous over other fracturing fluids. It is also stable in high temperature reservoirs (up to 300°F).

This study addresses one of the major issues on the performance of a tight gas producing well which is the effect of water blockage or APT on the productivity of those wells. Water blockage or water accumulation around the wellbore which is

introduced to the formation by water based drilling muds, completion fluids, stimulation fluids (i.e. spent acid) fracture fluids, workover fluids and kill fluids. They adversely affect the gas relative permeability curves, causing the water to be trapped inside the formation and handicapping its flow back with the producing gas, hence reducing the productivity and the performance of the tight gas wells.

Tight gas formations are characterized with low permeability, low porosity, higher capillary pressure, and high irreducible water saturation due to the nature of the small radii of curvature between the grains (due to the abundant presence of micro porosity) [3]. Tight formations are also characterized with low initial water saturation due to the desiccating effects on those reservoirs.

In tight gas formations, the water will remain immobile until it reaches the critical water saturation on the gas-water relative permeability curve, when that happens a significant drop in the gas permeability will happen impairing the mobility of the gas, a detailed explanation of the water blockage phenomenon will be discussed in the literature survey. A review on the fracturing fluids will also be discussed in the literature and the methods suggested to eliminate this effect.

GLDA (which is the main constituent of the newly proposed fracturing fluid) is a low IFT fluid, which will reduce the IFT eliminating the APT. At low pH GLDA reacts as an acid with the carbonate minerals in the formation producing CO_2 as a bi-product, and at high pH it will react with the rocks creating a lower IFT fluid than the initial value, which makes the fluid in both pH ranges effective in reducing the APT effect.

The new fluid system will be tested and evaluated in terms of rheology, fluid loss, and filter cake integrity against low and high permeability sandstones core samples

(Scioto and Berea). The fracturing fluid will be tested when diluted in both fresh water and seawater against several polymers with several concentrations and pH ranges. The results of this study will be the development and optimization of a new environmentally-friendly, cost efficient fracturing fluid for Acid/Proppant Fracturing. The developed fluid system will be tested on both low and high permeability sandstone core samples to evaluate its effectiveness.

CHAPTER 2

LITERATURE REVIEW

2.1 Fracturing Fluids (Hydraulic Fracturing/Acid Fracturing)

The difference between proppant fracturing and acid fracturing is the mean of which the induced fractures are kept open and prevent them from closing due to in-situ stresses. Proppant is used to prop the fracture open, while acid is used to unevenly etch the fracture surface to create conductive pathways.

Cross-linked gel fluids are used as a pad fluid which is injected to the formation to induce fractures as designed (height, width, and length). If proppant fracturing was chosen, a proppant will be injected in a viscos fluid with carrying capacity to the fracture system. However, if acid was chosen, the acid is then injected to create the uneven etches or channels, the acid can be either gelled, crosslinked or emulsified to reduce leak-off to the formation and prevent fluid loss.

2.1.1 Constituents of Fracturing Fluids

A typical fracturing fluid usually (shown in Table 2.1-2) contains 3 to 12 additives that are aimed to enhance the attributes of the fracturing fluid, such additives are like cross-linkers, buffers, breakers, clay stabilizers, gelling agents, etc. The constituents of fracturing fluids will be discussed further on, for instance friction reducers are added to the fracturing fluid and that is referred to by slick-water, biocides are added to prevent the

growth of micro-organisms which can cause precipitations or plugging issues, oxygen scavengers are also added to prevent corrosion of pipes (rust).

Commonly, fracturing fluids consists of 90% or more of fresh water and 8 percent of sand or proppant while the rest being the other additives needed to enhance the capabilities of this fluid, the resultant fracturing fluid should:

1. Have transportation abilities to carry the proppant to the fractures.
2. Be compatible with the formation and the fluid itself and not cause additional damage.
3. Withstand high enough pressure to propagate the fracture to the desired dimensions.
4. Prevent additional pressure drop due to friction losses.
5. Be environmentally friendly and not hazardous.
6. Break easily to allow for smooth cleanup and not cause retention of fluid loss.
7. Be cost efficient [5][6].

The constituents of a typical fracturing fluid are shown in Tables (2.1 & 2.2).

Table 2.1: Constituents of a typical fracturing fluid

Component / Category	Function / Remark
Biocide	Prevent microbial degradation
Breakers	Degrade thickener after job or disable cross-linker (wide variety of chemical mechanisms)
Ceramics	Proppant material
Clay stabilizers	For Clay bearing formations
Cross-linked gel systems	Increase viscosity
Cross-linkers	Increase the viscosity of the thickener
Defoamers	Break foams
Emulsifiers	For diesel premixed gels
Fluid-loss additives	Form filter cake, reduce leak-off in formation if thickener is not sufficient
Foamers	For foam-based fracturing fluids
Friction reducers	Reduce drag in tubing
Gel concentrates	Premixed gel on diesel base
Gel stabilizers	Keep gels active longer
Non-emulsifiers	Destroy emulations
Oil-based systems	Used in water sensitive formation
Oil-gelling additives	Same as cross-linkers for oil-based fracturing fluids
pH-control additives	Increase the stability of fluid (e.g., for elevated temperature applications)
Polymer plugs	Used also for other operations
Resin-coated proppants	Proppant material
Surfactants	Prevent water wetting of formation
Water-based gel systems	Common
Water-based polymers	Thickener, to transport proppant, reduces leak-off in formation

Table 2.2: Constituents of a typical fracturing fluid (Chemicals and their Common Applications)

Compound	Purpose
Acid	Helps dissolve minerals and initiate fissure in rock (Pre-fracture)
Ammonium Bisulfite	Removes oxygen from the water to protect the pipe from corrosion
Borate Salts	Maintain fluid viscosity as temperature increases
Citric Acid	Prevents precipitation of metal oxides
Ethylene Glycol	Prevents scale deposits in the pipe
Glutaraldehyde	Eliminate bacteria in the water
Guar Gum	Thickens the water to suspend the sand and transport it, also it reduces leak-off
Isopropanol	Used to increase the viscosity of the fracture fluid
N, n-Dimethyl Formamide	Prevents the corrosion of the pipe
Petroleum Distillates	Slicks the water to minimize friction
Polyacrylamide	Minimizes friction between fluid and pipe
Potassium Chloride	Creates a brine carrier fluid
Proppant	Allows the fissures to remain open so the gas can escape
Sodium Chloride	Allows a delayed break down of the gel polymer chains
Sodium or Potassium Carbonates	Maintains the effectiveness of other components, such as cross-linkers

Typical Solution used in hydraulic fracturing in Marcellus shale are shown in Table (2.3) [7].

Table 2.3: Constituents of a typical fracturing fluid (Marcellus Shale)

Constituents	Percentage
Water & Sand (Silica Sands)	99.51%
Acid	0.123%
Corrosion Inhibitor (N, n-Dimethyl formamide)	0.002%
Corrosion Inhibitor (Ammonium bisulfite)	-
Friction Reducer (Petroleum distillates)	0.088%
Friction Reducer (PAM)	-
Gelling Agent (Guar Gum/Hydroxyethyl cellulose)	0.056%
Clay Stabilizer	0.034%
Cross-linker (Borate Salts)	0.007%
Scale Inhibitor (Ethylene glycol)	0.043%
Breaker	0.009%
Iron Control (Citric Acid)	0.004%
Biocide (Glutaraldehyde)	0.001%
pH Adjusting Agent	0.01%
KCL (Brine)	0.06%
Surfactant	0.06%
Gel Stabilizer (NaCl)	0.01%
Gel Stabilizer (Na_2CO_3, KCO_3)	0.011%

Conventional fracturing fluids commonly used constituents are shown in Table (2.4) [8].

Table 2.4: Constituents of a typical fracturing fluid (Conventional Hydraulic Fracturing)

Constituents	Percentage
Water	99.2%
Acid	0.07%
Corrosion Inhibitor	0.05%
Friction Reducer	0.05%
Gelling Agent	0.5%
Clay Stabilizer	0.034%
Cross-linker	0.032%
Scale Inhibitor	0.023%
Breaker	0.02%
Iron Control	0.004%
Biocide	0.001%

Shale Gas Fracturing Fluid constituents are shown in Table (2.5) [8].

Table 2.5: Constituents of a typical fracturing fluid (Shale Gas)

Constituents	Percentage
Water	90.61%
Acid	0.11%
Corrosion Inhibitor	0.001%
Friction Reducer	0.080%
Gelling Agent	0.05%
Clay Stabilizer	0.034%
Cross-linker	0.006%
Scale Inhibitor	0.04%
Breaker	0.009%
Iron Control	0.004%
Biocide	0.001%
pH Adjusting Agent	0.01%
KCL	0.05%
Surfactant	0.06%
Sand	8.95%

A brief definition of some of the components used in fracturing fluids are given below along with some examples of those chemicals that are essential in designing a fracturing treatment:

- Cross-linkers

A cross-link is bonding two polymer chains to each other to modify the physical properties of the polymer. The bond between the polymer chains can be covalent or ionic bonds, cross-links are applied to both natural and synthetic polymers, and it happens as a result of chemical reaction initiated by applying pressure, heat, and change in pH or radiation. Cross-linkers are used to increase the molecular weight of the polymer, cross-linking increases the viscosity of the linear gel system from less than 50 cP to hundreds or thousands cP. In hydraulic fracturing the cross-linked gels are used to carry out the treatment of the rock and to support proppant transportation, it also increases the elasticity of the fluid.

Boron, zirconium, and titanium metals are used to cross-link gels such as Guar Gum and CMHEC gels, several other metals are used to cross-link Guar Gum such as aluminum and Chromium, and however they are not commonly used in the industry. Iron is also not used due to its damaging tendencies; iron precipitation is of a major concern in the stimulation industry and must be carefully accounted for. Each cross-linker has its own requirements, behavior and conditions for usage, but in common practices boron and zirconium are the widely used metals for cross-linking [9][10].

- Breakers

Oxidizers, acids and enzymes are additives that are usually added to the fracturing fluid to break or reduce the high viscosity of the fracturing fluid, it counters the effect of the cross-linkers to facilitates the clean-up process or the flow back of the fracturing fluid, the main issues in handling breakers are early breaking of the cross-linked gelled fluid

which will cause fluid loss or invasion to the formation, and late breaking of the cross-linked fluid which will cause plugging and retention of the residual polymer [9][10].

- Buffers

Are used to maintain the of pH at a certain level to allow for cross-linking of the polymer gels or hydration or dispersion. Buffers can be used to delay the crosslinking of the fluid till it reaches the desired depth because some of those buffers dissolve slowly. The most commonly used buffers in the industry are Sodium Hydroxide, Formic Acid, and Hydrochloric Acid [9][10].

- Biocides/Bactericides

Polymer degradation due to enzymatic attack of micro-organisms present in the water used to formulate the fracturing fluid is of a major concern. This attack causes the polymer life span to be shortened, hence, reducing the efficiency of the stimulation operation. Biocides are used to prevent this attack, while bactericides are used to prevent Sulfate Reducing Bacteria (SRB) from producing corrosive H_2S, as well as blocking the formation with the biofilm they produce on water wells. Chlorine dioxide is an example of an efficient biocide used in stimulation.

- Gel stabilizers

Used in stimulation to avert the degradation of a crosslinked gel due to divalent or trivalent ion contamination. This is of importance for high-temperature fracturing jobs. Sodium thiosulfate, Sodium gluconate, Sodium glucoheptonate, Diethanolamine, Triethanolamine, Methanol, Hydroxyethyl glycine, Tetraethylenepentamine,

Ethylenediamine are some of the gel stabilizers used in the industry (Crews & Huang) [9].

2.1.2 Water Usage in Hydraulic Fracturing

In 2010, it is estimated that 70 to 140 billion gallons of water are used to in the U.S to conduct fracturing operations on about 35,000 wells. It is estimated that fracturing operations in horizontal wells usually use from 500,000 to 1,000,0000 gallons of water for a single well, also for fracturing treatments on coalbed methane it is estimated that 50,000 to 350,000 gallons of water are used and for conventional vertical wells it is estimated that they use 200,000 gallons to 6,000,000 gallons of fresh water. Using such a huge amount of water has a great impact ecologically and environmentally, fresh water is usually obtained from drinking water aquifers, which causes great concern when addressing water supplies as well as the disposal of the used water which is not all the time environmentally friendly [11].

2.1.3 Candidate selection (Proppant-Fracturing vs Acid-Fracturing)

The most crucial factors affecting candidate selection for Proppant-Hydraulic-Fracturing are the formation permeability, reservoir pressure, existing skin in the vicinity of the wellbore, in-situ stress distribution in the reservoir, reservoir depth and the fracturing fluid viscosity. Reservoirs with a great amount of gas initially in place are considered the best candidate for stimulation by Proppant-Fracturing especially in tight formations where economic production is not possible by normal methods. The best candidate reservoirs are those with a substantial pay zone, medium or high pressure, barriers to minimize the growth of the fracture vertically (safety consideration) and substantial areal coverage. Whereas reservoirs not complying with those criteria are poor candidates, also

reservoirs with very low permeability (Ultra-Tight) are considered poor, because even if stimulated successfully they would not yield an economic producing rate [12].

On the other hand, the best candidate reservoirs for Acid-Hydraulic-Fracturing are those reservoirs characterized with low temperature, shallow depths and preferably carbonates since introducing acid to sandstone formations is often problematic. The range of temperature for the best candidates for this type of stimulation is less than 200°F, the reason behind this limit is because the nature of acid; an increase in the temperature increases the rate of reaction of the acid with the formation carbonate minerals allowing it to penetrate deeper into the fracture before becoming spent. Using a proppant with Acid-Fracturing is also not recommended since the fines resulting from the reaction are always released plugging the propping agent, hence, rendering the fracture less conductive. Cost efficiency and safety are always highly considered in this type of stimulation, for instance in deep high temperature reservoirs, additional huge cost is added due to the need of a reaction inhibitor for the acid, as mentioned, also handling the acid safely is of a major concern since these reservoirs large volumes of strong acids are required at a high pumping pressure and injection rates [12].

Economides et.al. (1989) Categorized fracturing fluids based on reservoir pressure and temperature, fracture half-length desired and the sensitivity towards water, the developed chart is depicted in Figure (2.1) [13].

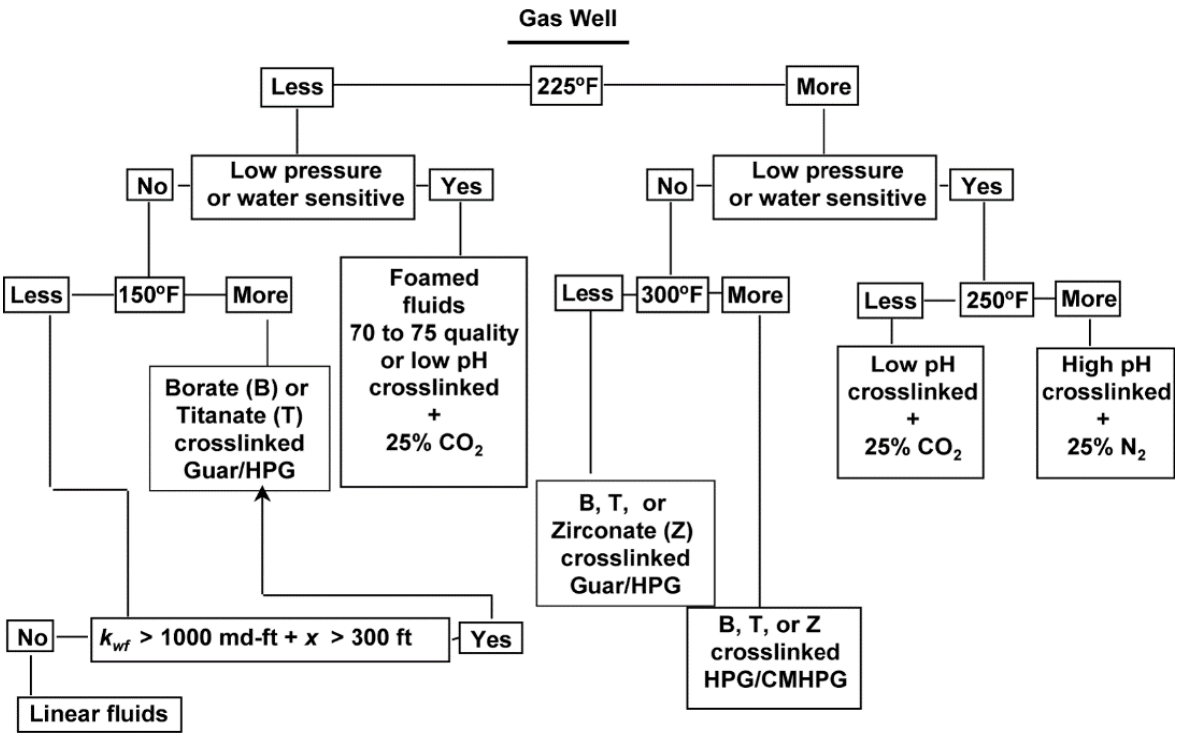

Figure 2.1: Selection of Fracturing Fluid for Gas Reservoirs[10]

Table (2.6) shows some of the most commonly used fracturing fluids and their conditions of usage.

Table 2.6: Fracturing Fluids and conditions for their use[10]

Base Fluid	Fluid Type	Main Composition	Used For
Water			
	Linear	Guar, HPG, HEC, CMHPG	Short fractures, low temperature
	Crosslinked	Crosslinker + Guar, HPG, CMHPG or CMHEC	Long fractures, high temperature
	Micellar	Electrolite + Surfactant	Moderate length fractures, moderate temperature
Foam			
	Water based	Foamer + N_2 or CO_2	Low-pressure formations
	Acid based	Foamer + N_2	Low-pressure, carbonate formations
	Alcohol based	Methonal + Foamer + N_2	Low-pressure, water-sensitive formations
Oil			
	Linear	Gelling agent	Short fractures, water-sensitive formations
	Crosslinked	Gelling agent + Crosslinker	Long fractures, water-sensitive formations
	Water emulsion	Water + Oil + Emulsifier	Moderate length fractures, good fluid loss control
Acid			
	Linear	Guar or HPG	Short fractures, carbonate formations
	Crosslinked	Crosslinker + Guar or HPG	Longer, wider fractures, carbonate formations
	Oil emulsion	Acid + Oil + Emulsifier	Moderate length fractures, carbonate formations

2.1.4 Fracturing Fluids used in the industry:

- Hydrocarbon based fluids:

Coşkuner (2006) stated that the use of hydrocarbon-based fluids has some benefits over the water-based ones, these benefits may include: Hydrocarbon-based fluids can be sold in the market or reprocessed easily, while the water-based fluids are usually disposed of, laboratory studies shown that the residue that results from the hydrocarbon-based fluids are less damaging than the one produced by the water-based fluids, and the cleaning up process of hydrocarbon-based fluids is easier. A field example was studied using a water-based fracturing fluid and a hydrocarbon-based one. The results show that using water-based fracturing fluids caused the reservoir to entrap water, hence reducing the gas flow after the flow back, which means that the relative permeability of gas is damaged due to the high water-saturation in the flushed zone, however using hydrocarbon based fluids yielded better results in regaining the permeability and increased gas flow, which means that there was no damage noticed from using such fluids with this formation [14].

- Polymers

Bennion (2004) mentioned in his paper polymers are used in tight gas formations for hydraulic fracturing, however, the relatively large polymer chains may introduce some damage in the formation by adsorption on the surface of the pores, restricting the flow of gas by reducing the relative permeability of gas in this obstructed formation by the adsorbed polymer. This damage however is not significant or apparent in higher quality formations but due to the limited permeability offered by the tight formations, it can have

a great effect on them, using oxidization agents may reduce the polymer adsorption effect [3].

- VES

Gupta (2009) stated that Viscoelastic surfactants are a combination of inorganic salts or surfactants with other surfactants, they have been widely used for several decades but its use as a fracturing fluid came around in the last decade, they increase the viscosity and elastic properties of the fluid, they are very efficient in proppant transportation due to their zero shear viscosity characteristics, they are classified into three main categories:

1. Vesicles.
2. Lamellar structures.
3. Worm-like micelles.

VES stable temperature range is normally from 160°F to 200°F, however adding high temperature stabilizers will increase that range to 250°F without foaming, they are easy to recycle, only a few additives are added without the hydration, thus they are simple fluid systems, they do not contain biopolymers so they do not require biocide, they also do not require additional surfactant to flow back, because they are low surface and interfacial tension fluids. They have properties similar to KCl brine, they don't need additional clay control additives. The viscosity of these fluids can be broken by altering the surfactants properties, or by changing the pH, salinity or by adding other hydrocarbons. The return permeability when using such fluids reported to approach 100% because of their wettability altering characteristics.

Adding foams to VES fluids such as nitrogen and carbon dioxide will make viscoelastic surfactant foams, the viscosity of the foam can be adjusted by modifying the VES base-viscosity and the quality of the foam, they are proved to be good fracturing fluids when APT is a possibility because they contain surfactants which will reduce the IFT hence these fluid systems overcomes capillary forces helping the recovery of hydrocarbon. VES fluids are usually used with coalbed methane wells [15].

- Emulsion of CO_2 with aqueous methanol based fluid

Gupta (2009) stated that substituting 40% of the water in the emulsion of CO_2 foams with methanol will reduce the APT when used with formation with sub-irreducible water saturation, these fluids yielded high viscosity of methanol fluids, these emulsions use surfactants which are compatible with methanol-based fluids, and they resulted in high return permeabilities when tested in the Canadian fields [15].

- Crosslinked foams

Gupta (2009) also said that Nitrogen and carbon dioxide were crosslinked to increase the stability of the fluids in high temperature formations or to minimize the amount of liquids injected in the formation, these fluids are crosslinked with zirconium fluids, and they are as effective as the 40% methanol containing CO_2 emulsions [15].

- Non-aqueous methanol fluids

Gupta (2009) stated that the advantage of using methanol-based fluids include low IFT, high water solubility, low freezing point, high vapor pressure and formation

compatibility, on the other hand the main concern of using such fluids is only related to safety precautions, and these are handled well using our modern technologies [15].

Increasing the viscosity of these methanol-based fluids was suggested in the literature, these include the addition of foaming the methanol or gelling them with synthetic polymers (Polyacrylamide and Polyethylene oxide), however Ely has described some limitations regarding the gelling of methanol based fluids: the ability to cross-link, the ability to break the polymer, temperature limits, and the solubility of these polymers in methanol [16].

Gupta (2009) has developed a fluid which consists of a modified guar dissolved in anhydrous methanol crosslinked with borate (at pseudo-high pH) or with zirconium (at pseudo-low pH), for CO_2 compatibility complexes and broken by an oxidizing breaker, this fluid has been successful in high pressure formations, it also can be energized with nitrogen or carbon dioxide

Bennion (2004) said that the use of gelled methanol have been successfully used but he noted that care should be taken in very low permeability formations (less than 0.1 mD) because adverse capillary effects can phase trap the alcohol, alcohol should also be avoided in reservoirs with liquid hydrocarbon saturation is known to occur, because low molecular weight alcohols (i.e. Methanol, etc.) can cause incompatibility problems with respect to sludge formation with crude oils because of their low degree of miscibility.

Bennion (2004) said that the injection of mutual solvents (methanol) with CO_2 is usually the most successful treatment for APT. He also said that the use of high molecular weight mutual solvents such as IPA and EGMBE in dealing with formations where liquid

hydrocarbon saturation is known to exist, they show greater miscibility and fewer incompatibility problems [3].

- Liquid CO_2-based fluids

Gupta (2009) said that to inhibit leak-off from the fracture face to the reservoir, fracturing fluid with viscoelastic properties must be used, liquefied CO_2 has very low viscosity. Low viscosity, low temperature fluids have higher leak-off rates, however the advantage of these fluids is that the fluid is compressible at high pressures, when it is pumped at a high pressure and low temperature, the fluid expands, this effect of thermal expansion inhibits the leak off near the fracture face [15].

Bennion (2004) suggested that CO_2 gas will dissolve in the trapped water in the flushed zone area giving it more energy to flow and due to its IFT reduction characteristics it will allow the flow of trapped oil easily, reducing the capillary pressure, hence the drawdown required would be much less.

Bennion (2004) recommended the use if CO_2 energized hydrocarbons or the straight version of it will yield better results as opposed to water-based fluids [3].

- Liquid CO_2-based foam fluids

Gupta (2009) said that several attempts has been made to increase the viscosity of the liquefied CO_2 as a base fluid by adding a foam of nitrogen as an external phase stabilized by a special foamers. The advantages of this fluid are to increase the viscosity and maintaining the conductivity and compatibility of these fluids [15].

- Gelled LPG

Gupta (2009) said that LPG gases are a mixture of petroleum and natural gases in a liquid state at ambient temperatures and moderate pressure (200 psi), the main advantages of using such fluids are: they are soluble in formation hydrocarbon, their density, viscosity, and surface tension are beneficial, the APT is practically eliminated and they approach 100% return permeability when using such fluids. He also said that formations with potential APT occurrence can be drilled, stimulated, or fractured using other than water-based fluids, to prevent impairing the flow of hydrocarbon due to APT.

Fluids with the fewest additives are the most cost efficient solution to fracture an unconventional formation, they however do not possess effective proppant transportation characteristics and they also are weak on leak-off control as well as friction problems especially if pumped wit high rates, using salt in fluids control the compatibility with clay containing formations [15].

Crosslinked water-based fluids and crosslinked oil-based fluids with borate or organometallic compounds aid in fracturing formation with high temperature, energized fluids with nitrogen or carbon dioxide can be also helpful in formation with high pressure, also to add leak-off control, foams of nitrogen or carbon dioxide may be used, if however the water-based fluids are incompatible with the formation, viscoelastic surfactants can be used, they have good proppant transportation features as well as they can be energized or foamed, methanol-containing fluids also can be used if the formation's incompatibility is due to capillary and unloading problems, and they can be replaced with crosslinked methanol-based fluids, CO_2-based fluids or LPG.

The main challenges in Hydraulic-Fracturing in tight formations are:

1. Aqueous Phase Trapping or water blockage.
2. Properties of the fracturing fluids.
3. Proppant (cost, materials).
4. Geology problem (subterranean formations, stress altered formations, ultra-low permeability).
5. Environmental impact (Chemicals).
6. Fracturing (Massive hydraulic fracturing, explosive fracturing, pneumatic fracturing, and sleeve fracturing).
7. Drilling (fracturing while drilling).
8. High Temperature / High Pressure stimulation.

2.2 Rheology of the Polymers used in Fracturing Fluids

Over the last three decades several publications were made focused on the development of new formulations or enhancing existing formulations to enhance the outcome of hydraulic fracturing which is a well-established operation aimed to enhance the productivity of oil and gas reservoirs, Guar-based polymers are still being used in the literature although it is less thermally stable in temperatures exceeding 300°F, and for the fact that on polymer loading Guar-based polymers cause residue damages on the proppant pack which damages the conductivity, thus, reducing the return permeability after the fracturing operations, for this, the research shifted towards using Polyacrylamides-based polymers for its thermal stability and less damaging properties,

PAMs are stable up to 450°F as reported in the literature. The research also focused on using less polymer concentrations to avoid damage on the conductivity of the fractures by the introduction of cross-linkers (Borates and Zirconium as an example), and the use of breakers to undo the cross-linking process, thus reducing the pumping rates required to pump these viscous fluids. In low permeability reservoirs, high viscosity fluids were no longer needed in order to minimize the leak-off, the use of slick water then emerged, however its carrying capacity is less than the conventional fracturing fluids, but it depends more on the velocity to carry the proppant with a limit of approximately 1lb/gal of proppant, of course at high velocities it is noteworthy that adding drag reducers is a must when dealing with such operations to minimize the friction resulting from high velocities [17].

A summary of the fracturing fluids used in the last decade is provided in Tables (2.7-2.8)

Table 2.7: Summary of the Fracturing Fluids in the last decade (Al Muntasheri 2014)

Fluid Type	Polymer Concentration, lb/1000 gal	Crosslinker Concentration, lb/1000 gal	Working Temperature Range	Reference
PAM-Based/Zirconium	66	3	269- 449.6°F (132-232°C)	Holtsclaw and Funkhouser (2010)
PAM-Based/Zirconium and activator	87	3.4 to 3.7	100.4- 269°F (38-132°C)	Holtsclaw and Funkhouser (2010)
Linear Biopolymer	40-70	-	<200°F (93°C)	Walters et al. (2009)
Low Molecular Weight HPG/Borate	Not Available	Not Available	200-275°F (93-135°C)	Weaver et al. (2002a and b)
AMPS-vinyl phosphonate/Zirconium	40	Not Available	425°F (218°C)	Gupta and Carman (2011)
Linear guar	33	0	<175°F (79°C)	Fakoya et al. (2013)
Guar/ boronic acid-functionalized nanoparticles	30	0.0166	100°F (37°C)	Lafitte et al. (2012)
VES (Quaternary ammonium)	Not Applicable	Not Applicable	<180°F (82°C)	Samuel et al. (1999, 2000)
VES (Amidoamine oxide)	Not Applicable	Not Applicable	<250°F (121°C)	Huang and Crews (2008)
VES Zwitterionic	Not Applicable	Not Applicable	<195°F (90°C)	Sullivan et al. (2006)
VES/CO_2 Emulsion	Not Applicable	Not Applicable	230°F (110°C)	Chen et al. (2005)

Table 2.8: Fracture conductivity data of proppant packs reviewed in the literature (Al Muntasheri 2014)

Polymer/Crosslinker Type	Polymer Content, lb/1000 gal	Breaker Content, gal/1000 gal	Closure Stress, psi	Shut-in Time, hours	Temperature	Regained Conductivity, %	Reference
PAM-Based/Zirconium	87	4	5,000	48	399°F (204°C)	68	Holtsclaw and Funkhouser (2010)
PAM-Based/Zirconium and activator	87	0.3 to 1.5	2,500	42-72	450°F (232°C)	34 to 100	Holtsclaw and Funkhouser (2010)
PAM-Based/Zirconium	66	5	4,000	71	399°F (204°C)	43-73	Holtsclaw and Funkhouser (2010)
PAM-Based/Zirconium	66	5	8,000	118	399°F (204°C)	39-47	Holtsclaw and Funkhouser (2010)
PAM-Based/Zirconium	66	5	10,000	165	399°F (204°C)	37	Holtsclaw and Funkhouser (2010)
Linear Biopolymer	40-70	Not Needed	6,000	Not Reported	200°F (93.3°C)	90	Walters et al. (2009)
Guar/Borate	NA	NA	6,000	Not Reported	200°F (93°C)	14	Walters et al. (2009)
AMPS-vinyl phosphonate/Zirconium	40	NA	3,000	24	425°F (218°C)	64-69	Gupta and Carman (2011)
AMPS-vinyl phosphonate/Zirconium	40	NA	3,000	24	385°F (196°C)	83	Gupta and Carman (2011)

2.3 Formation Damage

Formation damage is defined as any interaction between drilling, completion, or stimulation fluids and the formation/formation fluid, that might cause impairment to the reservoir, i.e. permeability reduction. Many field and research studies have assured that selecting the inappropriate completion fluid or additives is one of the main causes of formation damage that leads to permeability reduction in the vicinity of the wellbore and in some severe cases it might lead to losing the production. Basically, formation damage due to completion fluids occurs from the filtrate invasion into the formation, thus the only way to significantly mitigate the damage is to reduce the filtrate to the least possible amount using the suitable additives and formulation. Formation damage occurs in the forms of:

- Clay swelling
- Fines migration
- Emulsion and water blocks
- Scales precipitation
- Relative permeability effect
- Dissolution
- Plugging the formations due to improper operation conditions or introducing plugging materials [18].

2.3.1 Formation Damage in unconventional resources

Producing from unconventional resources (such as tight gas) is a great challenge to the petroleum industry, and that is due to the low permeability of these reservoirs which renders the normal production methods unsuccessful, large scale hydraulic fracturing or acid fracturing is required to produce at economic rates from those resources, and due to the nature of these reservoirs, permeability plays an important role in the production from these resources, which makes formation damage or permeability impairment the main concern when conducting such operations, it has been known that the damaging mechanisms resulting from fracturing operations include fluid invasion, fluid incompatibility resulting in precipitation of solids which causes plugging, hence, permeability impairment, proppant embedment which is defined as the process in which the proppant penetrates the soft formations during fluid leak-off to the formation in hydraulic fracturing operation, it reduces the fracture width, hence, reducing the resultant permeability of the formation after the stimulation process, gel residue in the proppant

pack and the formation of filter cake at the fracturing surface, which affects the fracture conductivity after the stimulation operation [19][20].

2.4 The Effect of Water-Blockage (Aqueous Phase Trapping)

2.4.1 Definition and theory

The initial water saturation is the saturation of water in a reservoir at the beginning of the drainage process or at the time when the reservoir is discovered. It depends on several parameters including depositional history, the geology of the formation, formation temperature, rock wettability, the pore-size distribution, and the height above the free water level in the formation. The initial water saturation can be equal to the Capillary Equilibrium Irreducible Water Saturation, can be higher or lower than it. On the other hand, the Capillary Equilibrium Irreducible Water Saturation exist on a reservoir by capillary mechanics. It depends on several parameters as well, such as pore size and pore throat distribution, wetting characteristics of the rock, reservoir morphology and the roughness of the surface. It signifies the water volume trapped at the corners of the grains and micro pores. In tight gas reservoirs, the initial water saturation tends to be less than the irreducible one due to the desiccation of the reservoir (sub-irreducible water saturation) and a number of other reasons. It is in that case when the productivity is low from the tight gas reservoirs. Figure (2.2) shows the mechanism of aqueous phase trapping [21].

Holditch suggested that the best method to analyze the effectiveness of a hydraulic fracturing clean-up process is to build a numerical simulation model. To investigate the

parameters affecting the flow between the fracture and the matrix, such as the water relative permeability, capillary pressure, reservoir damage and permeability hysteresis. He concluded from running the simulation model that if the permeability is not severely damaged by the invasion of fluid, no serious water block will occur (when the capillary pressure overcomes the drawdown pressure), if however, the formation is damaged and the capillary pressure in the damaged area increased, the water pressure in that area acts as sink drawing the water to the damaged area hence creating a water block [22].

Bennion (1994) suggested that Aqueous Phase Trapping can occur in the tight formation by several hypothesized factors or perhaps a combination of those factors, such as:

- Vaporization of water, potentially both pressure and temperature were low in the beginning of gas invasion, and due to the heat capacity of gas and the localized tectonic activities, high geothermal gradients were created which vaporized the water reducing it below the Capillary Equilibrium Irreducible Water Saturation.
- Pore geometry changes, over geological period, the overburden pressure is increased causing the pore geometry and size distribution to change, this effect coupled with the diagenesis of the reservoir would cause water blockage.
- Adsorption, clays, and minerals are water sensitive, adsorption of water would result in the removal of the effective water from the pore space.
- Irreducible saturation hysteresis effects, the existence of an initial wetting phase saturation in the formation may enhance the spontaneous imbibition of that fluid (make it more wetting). Cyclic hysteresis effects are caused

by the aqueous fluid invasion in a multiple manner, as well as the drainage cycle [21].

The severity of the Aqueous Phase Trapping depends on several factors including:

- The difference between the capillary equilibrium irreducible water saturation and the initial value of the water saturation, the greater this difference the larger permeability reduction takes place.
- The trend of the relative permeability curves of gas or oil phase with water, if the curve trend is relatively linear than the damage expected from the entrapment of water would be less than expected from a convex shaped curve.
- Saturation hysteresis can alter the value of capillary equilibrium irreducible water saturation by altering the contact angle hysteresis effect which is induced by cyclic saturation changes.
- The depth of invasion or filtrate invasion of the aqueous phase into the formation.

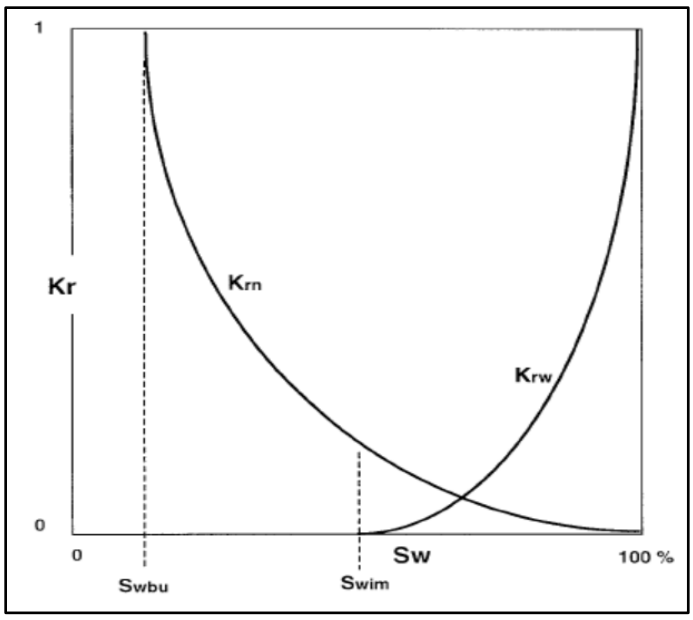

Figure 2.2: The Mechanism of Aqueous Phase Trapping

In summary, he suggested that the desiccating effect is caused by the increased temperature and pressure which will cause gas migration to isolated sediments, another mechanism that cause the desiccation of a reservoir is the imbibition of water into clays by the osmosis effect over a considerable geological time. Bennion (1994) developed a diagnostic empirical equation to assess the sensitivity of the formation to the aqueous phase trapping:

$$APT_i = 0.25\ log(k_a) + 2.2\ S_{wi}$$

Where APT_i is the aqueous Phase Trapping Index which normally ranges from 0.3 to 1, K_a is the formation uncorrected air permeability and S_{wi} is the initial water saturation (and not the irreducible one).

Figure (2.2), shown above, is an example set of relative permeability curves, thorough investigation of this figure shows that if the zone of interest has a saturation value greater

than 45% of the irreducible value trapping would not be problematic, because the formation is highly saturated with water. The figure also shows that if an aqueous fluid is to be introduced to a desiccated formation it would spring back to the value of irreducible water saturation.

Coşkuner (2006) suggested that the water blocks occur when a water based fluid is injected into the formation, this will cause a large gradient of the capillary pressure between the invaded zone and the uninvaded zone, the formation will act to this huge gradient by equalizing the pressure in each zone , with that the water is then redistributed or imbibed away from the invaded zone and away from the fracture face, the saturation in the flushed area, however can only be reduced to the capillary equilibrium irreducible water saturation, and that means that there still might be water blocks, also when that happen the speed of imbibition will decrease as the absolute permeability of the formation decreases, this effect is also coupled with the flow of gas (if the well is set on production) acting on the opposite direction of the imbibition process, hence slowing the equalization more [14].

Crotti (2007) did not acknowledge the idea of a sub-irreducible water saturation, he suggested that the reason behind the less initial water saturation and higher capillary pressure is having an over-pressurized reservoir, or a reservoir that did not reach equilibrium, which will lead to an increase in pore volume hence, a decrease in initial water saturation, over-pressurizing a reservoir will cause the rock and water to compress, and while the rock compressibility is higher than that of water, that means that it will compress more than water which will allow the pores to be relatively larger, and will lead to a reduction of the water saturation, moreover, this reduction in water saturation will

reduce the relative permeability of the gas drastically, and will negatively affect the production of gas in tight formations. Crotti built a simple non-equilibrium model explaining all characteristics of a typical tight gas reservoir, he concluded that these reservoirs have no transition zones, he also suggested that the free water level is non-sense concept when dealing with tight gas reservoirs, he suggested that the original gas in place should be correctly estimated to avoid the use of free water level as a method of determining the saturation value of the aqueous phase present in these reservoirs [23].

Aguilera suggested that tight gas reservoirs are formed throughout geological time, the net average stress increases rapidly, dominated by some main process such as de-watering, permeability and porosity reduction and gas generation and migration all which are controlled by in-elastic processes [4].

Gupta suggested that the fluid retention is caused by the formation capillary forces, which is the change in pressure between the wetting phase (water) and the non-wetting phase (gas). Sub-irreducible water saturation exists in tight formation by a number of factors such as the dehydration, desiccation, compaction, mixed wettability effects, considerable height above free water level (due to drainage), and diagenesis occurring over some geological period. Sub-irreducible water saturation cause the imbibition effects to have a severe effect on the tight gas formations [15].

Adverse capillary forces result in high in-situ saturation of trapped liquid hydrocarbon or water which causes serious production impairment. Low permeability reservoirs are sensitive to capillary retention effects, rock-to-fluid and fluid-to-fluid compatibilities, Injecting water based fluids in tight formations with higher capillary pressure will cause

imbibition of these fluids and entrapment, creating a water block in the form of high water saturation zone near the wellbore (near the fracture face area) restricting the flow of gas from the tight formation.

Bahrami (2011) conducted simulation modelling to evaluate the effect of water blocks in tight formation and the influence on core flow and well productivity, he suggested that during drilling operations the injected drilling fluids usually forms a filter cake around the wellbore stopping the invasion of fluids into the formation, however in tight formations, liquid invasion lasts for a longer periods of time due to the weak mud cake formed, deeper invasion of fluids also might occur due to the low matrix porosity and strong capillary pressure in tight formations, during the invasion of liquids into the formation, water saturation is increased from the initial water saturation to a higher value in the vicinity of the wellbore, and as gas is being produced during the clean-up process, the water saturation is reduced from that higher value to the irreducible water saturation, this process is followed by a decreased gas flow rate due to the reduction of relative permeability of gas and the permeability of the invaded zone. He concluded that to produce gas, reservoir pressure should be sufficiently high (higher than the formation capillary pressure) to recover the liquid invaded into the formation [24].

Assiri (2014) conducted a numerical investigation on the performance of a desiccated tight reservoir using a commercial simulator to study the effect of water blockage, he then concluded that the if water is introduced to those reservoirs during drilling or hydraulic fracturing, gas rates will significantly drop due to the blockage of water, which supports the existence of the desiccation effect, he suggested that the clean-up process of water blocks is highly dependent on the degree of desiccation of the tight gas formation.

He also concluded that although the results of running the simulation with injection of water and without the injectants are very close, the produced gas is delayed and will impact the economics of the producing field [2].

2.4.2 Minimization of Water Blockage effect

Tight gas formations, as previously mentioned, are very susceptible to damage due to its very low permeability, these formations can only withstand minimal formation damage. These formations are sensitive to phase trapping effects; hence the compatibility of the rock and fluid systems represent a great concern.

As mentioned above in the previous section, aqueous phase trapping is regarded to be a major mechanism of damage in tight formations, the following are some of the potential solutions found in the literature to minimize the Aqueous Phase Trapping effect:

In drilling, completion or even fracturing operations, the use of hydrocarbon-based fluids is preferred over the water-based fluids, although hydrocarbon –based fluids may also cause retention to some degree, but in general, the amount of phase trapping that could occur from such fluids would be very small compared to the water-based fluids. Hydrocarbon-based fluids are miscible with the hydrocarbon system which will eliminates any possibility of Aqueous Phase Trapping (that is if fluid does not cause any incompatibility issues with the formation itself). This is due to the fact that the hydrocarbon in that case would be the non-wetting phase, and since there will be no hydrocarbon saturation existing in the vicinity of the wellbore (or a small amount), the damage would be significantly less. If, however the hydrocarbon partially or totally wet

the formation itself, those fluids may be not beneficial over the water-based fluids, as the formation in that case will trap additional hydrocarbon due to spontaneous adhesion.

Using hydrocarbon-based fluids however is not applicable if the formation permeability is very low it causes great capillary retention of hydrocarbons, the hydrocarbon present in the formation is the main wetting phase or it is partially wetting or if the reservoirs contained oil-wet minerals such as pyro-bitumen, graphite, talc, coal, sulphur, sulfides).

If, however water-based fluids must be used or they are the only economically feasible solution, few considerations must be cared for to restrict or minimize the severity of the phase trapping:

- Balanced, Under-balanced or air drilling operations.
- The use of gaseous-based fracturing fluids.
- The use of low-fluid-loss system of fluids in hydraulic fracturing operations (minimizing fluid invasion).
- Artificial bridging agents.

2.4.3 Remediation (Removal) of Water Blockage effect

Coşkuner suggested that process of clean-up of the water retained can be achieved more quickly if the initial water saturation is close to the irreducible water saturation of the flushed zone area, the clean-up process is carried out by two regimes: displacement of water blocks by the gas existing in the formation, and the vaporization of the remaining water by the gas flow due to the decrease in pressure when it becomes under-saturated [14].

Bennion gave a few solutions to remove the phase traps if it occurred in low permeability formations, he suggested that:

- Increasing the drawdown pressure across the water blocked zone will lower the water saturation in that zone, due to the fact that the saturation in that zone is a function of capillary gradient applied, this solution however has many shortcomings including the fact that the reservoir has to be free from fines migration or potential coning problems or condensate dropout potential, also this solution cannot be implemented in normal fields due to the high required drawdown to remove the phase trap present.
- Reducing the IFT between the gas and water systems will directly reduce the capillary pressure since it is a straight function of it, hence reducing the IFT between the gas and the pore space will mobilize the gas easier with the existing drawdown pressure, to reduce the IFT some additives are used such as: Surfactants, mutual solvents such as methanol or EGMBE which reduces the IFT and are mutually miscible in the water system as well as the gas system, they also reduce the viscosity and increase the vapor pressure and volatility which aids in the vaporization of the water trapped in the system, CO_2 is also used for water blocks due to its known ability of reducing the IFT and its ability to dissolve in the trapped liquid, extract the trapped water as a desiccant as well as to provide it with energy to obtain a high gradient of capillary forces, dry gas, liquefied carbon dioxide, liquefied petroleum gas, liquefied and ethane are also used to remove water blocks from hydrocarbon-

based traps, they generate miscibility with the trapped hydrocarbon depending on the pressure and the pressure of the system.

- Changing or increasing the radii of curvature of pores (Pores geometry) can make the pore less constrictive reducing the capillary pressure and allow more flow of hydrocarbon, the injection of weak acids accomplishes this such as HF, however the injection of acids can aggravate more formation damage than curing the existing, also it may be trapped as well if it invaded beyond the zone of reaction.
- Direct removal of water blocks by saturation with hydrocarbons, and its done by several techniques including:

  i. Dry gas injection, dehydrated injection of gas will result in the desiccation of the zone near the injection (flushed zone), causing the vaporization of the water present in this flushed zone, the goal of that injection is to dehydrate some of the highly conductive channels to insure a conductive flow path for the gas flow, it is widely used in horizontal wells, in some cases adding mutual solvents which increase the ability of extraction, other dry gases may be used such as N_2, O_2, CO_2 or dehydrated flue gas, an example of mutual solvents is methanol.

  ii. Heat treatment and air injection.

  iii. Other methods to remove APT are constructed based on generating heat in-situ, which will desiccate the formation or dry it by vaporizing the water blocks trapped inside the formation.

  iv. Hydraulic fracturing bypassing the water trapped area [25].

CHAPTER 3

RESEARCH OBJECTIVES AND METHODOLGY

3.1 Research Motivation

In tight gas formations water is typically the wetting phase, when the reservoir is under-saturated, the capillary pressure therefore becomes high it tends to imbibe and entrap water into the pores of the formation, defining this formation as a desiccated one (thirsty reservoir). The pore system now has a lower initial water saturation than the irreducible water saturation and has a large cross-sectional area of the pore throat which allows the flow of gas. If a fluid was introduced to this formation, the water saturation will increase to a value higher than the irreducible water saturation, resulting in the entrapment of water in the damaged zone or flushed zone, hence, a decrease in the flow of gas produced will occur. Flowing back the system will return the water saturation to a value not lower than capillary equilibrium irreducible water saturation value, this behavior is dictated by the geometry of the pores' capillarity, resulting in the entrapment of water in that formation. The increase in the water saturation near the wellbore (flushed zone) due to water entrapment is called the Aqueous Phase Trapping effect. However, the flowing back process usually takes time, more time is also expected in tight formations since the permeability of the formation is very low.

Reducing the IFT between the gas and water systems will directly reduce the capillary pressure, since it is a straight function of it, meaning, the reduction of IFT between the

gas and the pore space will mobilize the gas easier with the existing drawdown pressure minimizing the Aqueous Phase Trapping effects.

In Hydraulic-Fracturing operations (Acid or Proppant), water is mixed with a gelling agent and a cross-linker and is used as a pad fluid to breakdown the formation (to initiate fracture). A water-based fluid is then injected to propagate the fracture height, length and width, acid is then injected into the formation (fracture face) to etch the walls of the fracture creating a conductive fracture or a proppant to keep the fracture from closing, and rarely both proppant and acid are used. To minimize fluid leak-off the fluid is usually gelled with an agent, cross-linked or emulsified, a great number of fluid additives are added to the fracturing fluid due to that, especially in tight formation where the permeability of the formation is low, and cannot produce unless it is stimulated.

The fracturing fluid mainly consists of fresh water, Proppant, Acid, cross-linker, breaker, buffer, stabilizer, biocide and a gelling agent, which sometimes makes the fluid extremely complicated in handling or mixing, not to mention that it becomes costly sometimes, also there are some issues regarding the cross-linkers and the breakers as it was mentioned in the literature review, GLDA has been used successfully to stimulate sandstone formations (Acidizing) and has proven from our preliminary laboratory experiments that it works as an acid, a cross-linker, and biocide for the polymer, it also has breaking capabilities which when used as a fracturing fluid would reduce the number of additives in the fracturing fluid and would render it simple and cost efficient as well as effective as to be seen from this study. It also works under low pH as an acid (i.e. pH 4) or at high pH (i.e. pH 12) as a chelating agent. It removes carbonate minerals (damaging minerals) from illitic sandstones effectively.

GLDA is also a low IFT fluid, and as an acid it also produces CO_2 as a bi-product which can, as result, reduce the IFT, and at high pH it will react with the salts creating a lower IFT fluid than the initial, hence minimizing the Aqueous Phase Trapping (Water Blockage) effect which is regarded to be a major mechanism of damage in tight formations.

3.2 Research Objectives

The main objectives of this study are to:

1. Develop a simple-fluid system for Hydraulic-Fracturing (at high pH) purposes, that consists of Chelating agents (which works as an acid, cross-linker, breaker, and biocide for the polymer), gelling agents (HPAM, Co-Polymer (AMPS), Xanthan, Thermoviscosifying-Polymer (TVP) & Hydroxypropyl Guar (HPG) were tested and evaluated) using seawater and fresh water (Table 3.1).
2. Evaluate the developed fluid in terms of:
    - Stability in high pressure high temperature high pressure conditions, breaking and cross-linking efficiency (Delay Time).
    - Rheological properties.
    - Return permeability of the core samples after flooding, to determine the effectiveness of the flow-back process.
3. Study the effect of seawater on the performance of the developed fracturing fluid as opposed to using fresh water, and investigate the reactions occurring on both fluid systems.

Table 3.1: A comparison between the conventional Fracturing Fluid and the proposed fluid

Current Fracturing Fluids constituents	Proposed Fracturing Fluid Fluid constituents
• Buffer • Acid • Biocide • Clay Stabilizer • Gel Stabilizer • Cross-linker • Breaker • Surfactant (IFT Reducer) • Fresh Water • Polymer (Gelling Agent)	• Chelating Agent • Fresh water / Seawater • Polymer (Gelling Agent)

The benefits of this study are as follows:

1. The proposed fluid will replace 8 additives that are essential to the fracturing fluid.
2. The proposed fluid will enable us to use either Seawater or Fresh-water which is very cost efficient and readily available.
3. Chelating agents at low pH acts as an acid which contacts large surface area on the fracture surface by etching and it will yield bigger surface area. At a high pH it will create dissolution which will enhance the surface area.
4. Chelating agents have been proven to eliminate carbonate minerals effectively which are present in the pore spaces, this property will aid in making a more conductive fracture and allow more diffusion and flow of gas.
5. The fluid Stability is controlled by the concentration of the Chelating agents as opposed to the current fracturing fluids which need a stabilizing agent.

6. The proposed fluid will act as a thickening agent to increase the viscosity to the desired values and as a breaker to the polymer and that will aid in flowing back easily without plugging.
7. Chelating agents is a low IFT fluid and when it reacts (at low pH) as an acid it produces CO_2 as a bi-product, and at high pH it will react with the salts creating a lower IFT fluid than the initial. So, the developed fluid will significantly reduce the IFT, and at high pH it will react with the salts creating a lower IFT fluid than the initial value it eliminating the Aqueous Phase Trapping Effect.
8. The proposed fluid is environmentally friendly and can be disposed easily.

3.3 Methodology and Apparatus

As mentioned, the objective of this study is to develop and evaluate a simple fluid system for hydraulic fracturing purposes at high pH (Proppant Fracturing), to achieve those objectives the study was carried out and divided into four sections as it will be shown and elaborated.

3.3.1 Polymer Stability and Tolerance Study using Fresh water and Seawater

This section discusses the evaluation of the thermal stability of the polymers which was used in the study and the effect of the seawater minerals on the stability of the polymers as well as the evaluation of the functioning groups of each polymer and its effect on the thickening of the developed fracturing fluid using the previously mentioned formulation.

- Thermogravimetric Analysis (TGA):

Thermogravimetric Analysis is a technique in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled

temperature program in a controlled atmosphere. SDT-Q600 (shown in Figure 3.3) instrument was used to conduct the TGA experiments, one set of experiments was conducted on this instruments as the Table (3.2) shows.

Table 3.2: TGA Thermal stability survey scan

#	Polymer Type	Temperature Range (°F)	Polymer Weight (mg)	Rate of temperature increase (°F/min)	N_2 flow rate (mL/min)
1	HPAM	77 - 350	25	9	20
2	AMPS	77 - 350	25	9	20
3	Xanthan	77 - 350	25	9	20
4	HPG	77 - 350	25	9	20
5	TVP	77 - 350	25	9	20

This set was conducted to determine the tolerance of the polymer or the stability of the polymer when subjected to elevated temperatures with time before it starts to degrade, the specific temperature range which were used was chosen based on the range of temperatures which can be encountered in high temperature reservoirs which usually ranges from 200°F to 300°F

- Fourier Transform Infrared Spectroscopy (FTIR):

Is a technique which is used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. An FTIR spectrometer simultaneously collects high spectral resolution data over a wide spectral range. BRUKER TENSOR27 was the instrument used to conduct the FTIR experiments Figure (3.4), The experiments conducted are

shown in Table (3.3) and the operational parameters are shown in Table (3.4). The reason behind those experiments is to explain the thickening-breaking mechanism and the effect of the pH and temperature have on the thickening-breaking mechanism, by monitoring the functional groups in each of the cases to understand the chemical reaction occurred in the developed fracturing fluid.

Table 3.3: FTIR experiments list

#	Experiment
1	20 wt.% of GLDA Solution at pH 4
2	20 wt.% of GLDA Solution at pH 12
3	45 pptg of AMPS diluted in DI water
4	45 pptg of AMPS diluted in Seawater
5	20 wt.% of GLDA at pH 12 mixed with 45 pptg of AMPS diluted in DI water (after Thickening)
6	20 wt.% of GLDA at pH 12 mixed with 45 pptg of AMPS diluted in DI water (after Breaking)
7	20 wt.% of GLDA at pH 12 mixed with 45 pptg of AMPS diluted in Seawater (after thickening)
8	20 wt.% of GLDA at pH 12 mixed with 45 pptg of AMPS diluted in Seawater (after Breaking)

Table 3.4: FTIR Operational Parameters

Operational Parameters	
Number of scans	8
Resolution	4 cm^{-1}
Scan Speed	10 KHz
Scan Range	400 cm^{-1} – 4000 cm^{-1}

3.3.2 Development of the Fracturing Fluid Using Fresh Water

This section discusses the rheological properties of the developed fluid when subjected to high pressures, high temperatures and/or high shear rates conditions and the effect of other fluid properties such as concentrations, pH, and polymer types on the stability of the developed fluid, this rheological study was conducted as follows:

1. The sample was prepared using the predetermined ratios (shown on the following sub-sections), and mixed using a fluid mixer (shown in Figure 3.5).
2. 50 cc were taken from the sample and loaded up in the rheometer's cup and closed firmly, Grace m5600 Rheometer (shown in Figure 3.7) was used in this study for rheological measurements.
3. The pressure of the system was then raised to the predetermined pressure point.
4. The bath was attached to the rheometer and heated to the predetermined temperature point.

5. The experiment conditions were then set on the rheometer's computer, and ran for the predetermined time.
6. After the experiment is done, the system was then flushed from any residual fluid on the lines and cleaned thoroughly, preparing the system to load another sample, repeating the previously mentioned steps again.

The following sub-sections elaborate the constituents and proportions of the developed fluid and the various conditions of which the rheological experiments were conducted at:

- Chelating agents type and Polymer type screening:

Three samples of 0.43 wt.% of XC polymer each mixed with a different type of 20 wt.% of Chelating agent (GLDA, DTPA, and EDTA) at pH 12 using fresh water, the temperature was 200°F and a shear rate of $170s^{-1}$. Then the rheological profiles of the three experiments were measured with time to evaluate the viscosity behavior of the fluid. The purpose of this screening is to screen out the less effective chelating agents in terms of the thickening-breaking behavior that occur in the fluid samples. The conditions of the experiments are elaborated in Table (3.5).

Table 3.5: Chelating agents screening experiments' conditions

#	Chelating Agent Type	Chelating Agent Concentration (wt.%)	Polymer Type	Polymer Concentration (wt.%)	Temperature (°F)	Shear Rate (s^{-1})	pH	Running Time (hrs)
1	GLDA	20	XC	0.43	200	170.3	12	40
2	EDTA	20	XC	0.43	200	170.3	12	40
3	DTPA	20	XC	0.43	200	170.3	12	40

Five samples of 20 wt.% of GLDA, each mixed with one gelling agent (AMPS, HPAM, XC, TVP and HPG), with a concentration of 20 pptg for each polymer using Fresh water (Deionized Water). Then the rheological profiles of the five experiments were measured with time to evaluate the viscosity behavior of the fluid. The purpose of this screening is to determine the tolerance and stability of each polymer with GLDA and to evaluate the thickening-breaking time of each polymer with GLDA. The conditions of the experiments are elaborated in Table (3.6).

Table 3.6: Polymer screening experiments' conditions

#	Polymer Type	Polymer Concentration (pptg)	Temperature (°F)	Pressure (Psia)	Shear Rate (s^{-1})	pH	Running Time (hrs)
1	AMPS	20 (0.239g)	300	300	511	12	12
2	HPAM	20 (0.239g)	300	300	511	12	12
3	Xanthan	20 (0.239g)	300	300	511	12	12
4	Guar Gum	20 (0.239g)	300	300	511	12	12
5	TVP	20 (0.239g)	300	300	511	12	12

- Rheological properties:

In this section the effect of Temperature, GLDA Concentration, Polymer Concentration, Shear rate and pH on the rheological properties of the developed fracturing fluid were studied using GLDA, AMPS and fresh water, the study was conducted in certain conditions as shown in Tables (3.7-3.11).

Table 3.7: The effect of the pH of GLDA

#	pH	Polymer Concentration (pptg)	GLDA Concentration (wt.%)	Temperature (°F)	Pressure (Psia)	Shear Rate (s^{-1})	Running Time (hrs)
1	4	20 (0.239g)	20	200	300	511	12
2	7	20 (0.239g)	20	200	300	511	12
3	12	20 (0.239g)	20	200	300	511	12

Table 3.8: The effect of temperature

#	pH	Polymer Concentration (pptg)	GLDA Concentration (wt.%)	Temperature (°F)	Pressure (Psia)	Shear Rate (s^{-1})	Running Time (hrs)
1	12	20 (0.239g)	20	77 (Room)	300	511	12
2	12	20 (0.239g)	20	200	300	511	12

Table 3.9: The effect of polymer concentration

#	pH	Polymer Concentration (pptg)	GLDA Concentration (wt.%)	Temperature (°F)	Pressure (Psia)	Shear Rate (s^{-1})	Running Time (hrs)
1	12	20 (0.239g)	20	200	300	511	12
2	12	70 (0.839g)	20	200	300	511	12

Table 3.10: The effect of GLDA concentration

#	pH	Polymer Concentration (pptg)	GLDA Concentration (wt.%)	Temperature (°F)	Pressure (Psia)	Shear Rate (s^{-1})	Running Time (hrs)
1	12	45 (0.539g)	5	300	300	511	12
2	12	45 (0.539g)	10	300	300	511	12
3	12	45 (0.539g)	20	300	300	511	12
4	12	45 (0.539g)	30	300	300	511	12
5	12	45 (0.539g)	40	300	300	511	12

Table 3.11: The effect of shear rate

#	pH	Polymer Concentration (pptg)	GLDA Concentration (wt.%)	Temperature (°F)	Pressure (Psia)	Shear Rate (s^{-1})	Running Time (hrs)
1	12	20 (0.239g)	20	300	300	100	12
2	12	20 (0.239g)	20	300	300	511	12

3.3.3 Development of the Fracturing Fluid Using Seawater

- Seawater formulation

In this section the effect of seawater minerals on the performance of the developed fluid has been studied to determine the viability and compatibility of this fluid to seawater.

The Arabian Gulf Seawater was used in this study and was formulated using the following mineral composition and concentration, (Tables 3.12 & 3.13).

Table 3.12: Ions of Solids dissolved in the Arabian Gulf Seawater

Ions	Seawater
Sodium	18300
Calcium	650
Magnesium	2110
Sulfate	4290
Chloride	32200
Carbonate	0
Bicarbonate	120
TDS	57670

Table 3.13: The Salt Recipe for Arabian Gulf Seawater

Salts	Seawater
NaCl, g/L	41.041
$CaCl_2.2H_2O$	2.384
$MgCl_2.6H_2O$, g/L	17.645
Na_2SO_4, g/L	6.343
$NaHCO_3$, g/L	0.165

- Rheological properties:

In this section the effect of Temperature, GLDA Concentration, Polymer Concentration, Shear rate and pH on the rheological properties of the developed fracturing fluid were studied using GLDA, AMPS and Seawater, the study was conducted in certain conditions as shown in Tables (3.14-3.17).

Table 3.14: The effect of the pH of GLDA

#	pH	Polymer Concentration (pptg)	GLDA Concentration (wt.%)	Temperature (°F)	Pressure (Psia)	Shear Rate (s^{-1})	Running Time (hrs)
1	4	20 (0.239g)	20	200	300	511	12
2	7	20 (0.239g)	20	200	300	511	12
3	12	20 (0.239g)	20	200	300	511	12

Table 3.15: The effect of temperature

#	pH	Polymer Concentration (pptg)	GLDA Concentration (wt.%)	Temperature (°F)	Pressure (Psia)	Shear Rate (s^{-1})	Running Time (hrs)
1	12	20 (0.239g)	20	77 (Room)	300	511	12
2	12	20 (0.239g)	20	200	300	511	12

Table 3.16: The effect of polymer concentration.

#	pH	Polymer Concentration (pptg)	GLDA Concentration (wt.%)	Temperature (°F)	Pressure (Psia)	Shear Rate (s^{-1})	Running Time (hrs)
1	12	20 (0.539g)	20	200	300	511	12
2	12	70 (0.839g)	20	200	300	511	12

Table 3.17: The effect of GLDA concentration (Diluted with Seawater)

#	pH	Polymer Concentration (pptg)	GLDA Concentration (wt.%)	Temperature (°F)	Pressure (Psia)	Shear Rate (s^{-1})	Running Time (hrs)
1	12	45 (0.539g)	5	300	300	511	12
2	12	45 (0.539g)	10	300	300	511	12
3	12	45 (0.539g)	20	300	300	511	12
4	12	45 (0.539g)	30	300	300	511	12
5	12	45 (0.539g)	40	300	300	511	12

3.3.4 Characterization and Evaluation of the Developed Fracturing Fluid on Sandstones

- Core preparations:

A 2.5-inch in diameter, 2-inches in length sandstone cores were cut, polished and the end faces were grinded, two samples have been prepared from different sandstones varying in permeability (See Table 3.18 for core properties). The three core samples are saturated in 3 wt.% Potassium Chloride KCl (Brine water) to prevent damage occurring from clay minerals if contacted by fresh water. The preparations of the cores were as follows:

1. The cores were dried from any water or humidity retained in an oven (250°F) for 24 hours.
2. The dry cores were weighted using a weight balance shown in Figure (3.4).
3. The cores were then saturated with brine under vacuum using a pump and a desiccator for 6 hours.

4. The saturated cores were then weighted and the porosities of the cores were calculated.
5. The cores' permeabilities were then calculated using Darcy's law.

Table 3.18: Core samples specifications

Core sample Type	Permeability
Berea sandstone	150 - 200 mD
Scioto sandstone	3 - 7 mD

- Fracturing Fluid Preparations:
    1. For Scioto sandstone core samples: 350 ml of 20 wt.% GLDA at pH 12 and 45 pptg of AMPS (Co-Polymer) diluted in DI water were prepared for the continuous pumping experiment.
    2. For Berea sandstone core sample: 350 ml of 20 wt.% GLDA at pH 12 and 70 pptg of XC-Polymer diluted in DI water were prepared for the continuous pumping experiment.
- Filter-Press with continuous pumping set-up:

The continuous pumping filter press set up is shown on the following schematic (Figure 3.1 & 3.2)

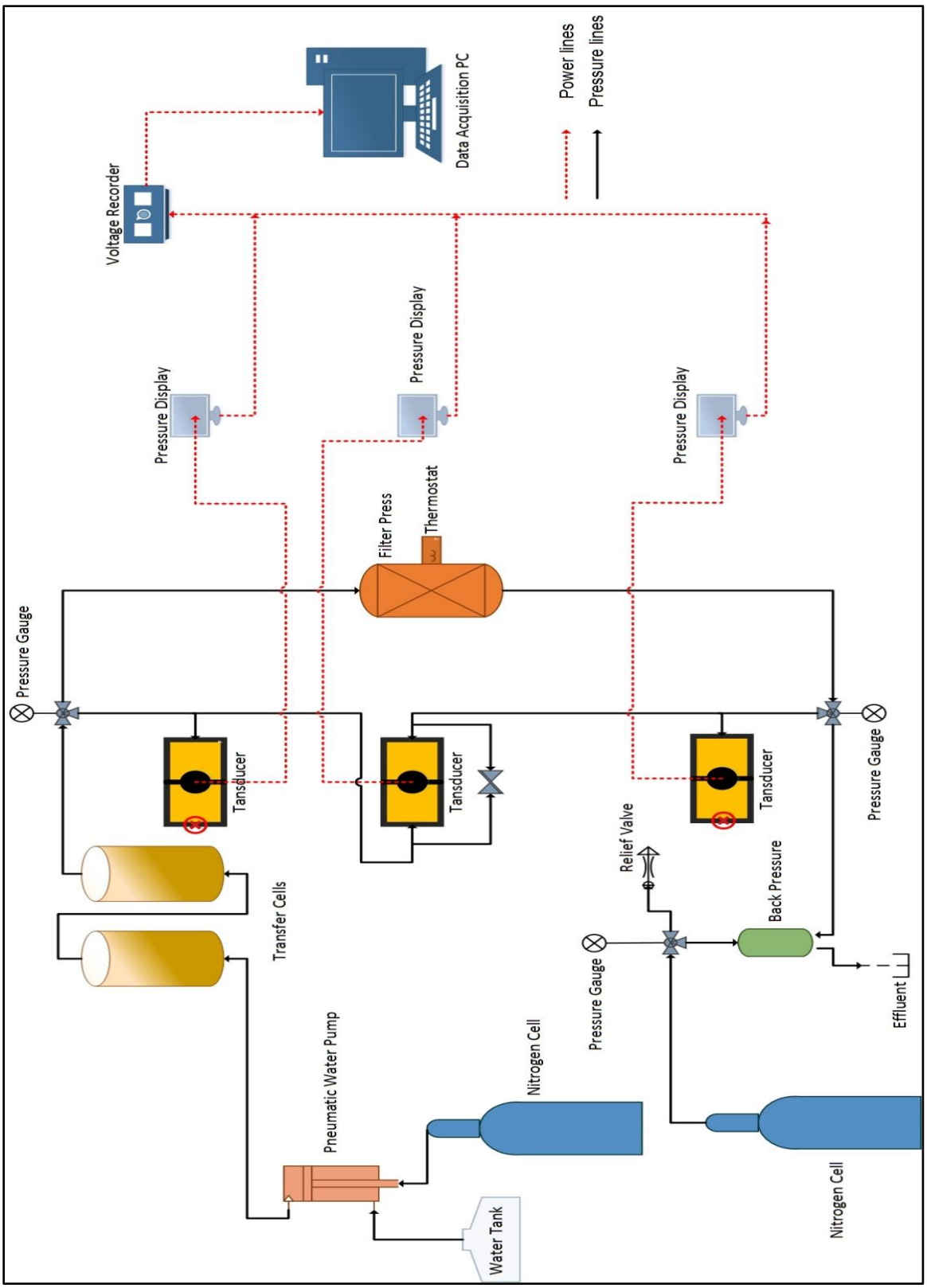

Figure 3.1: Filter-Press with continuous pumping set-up

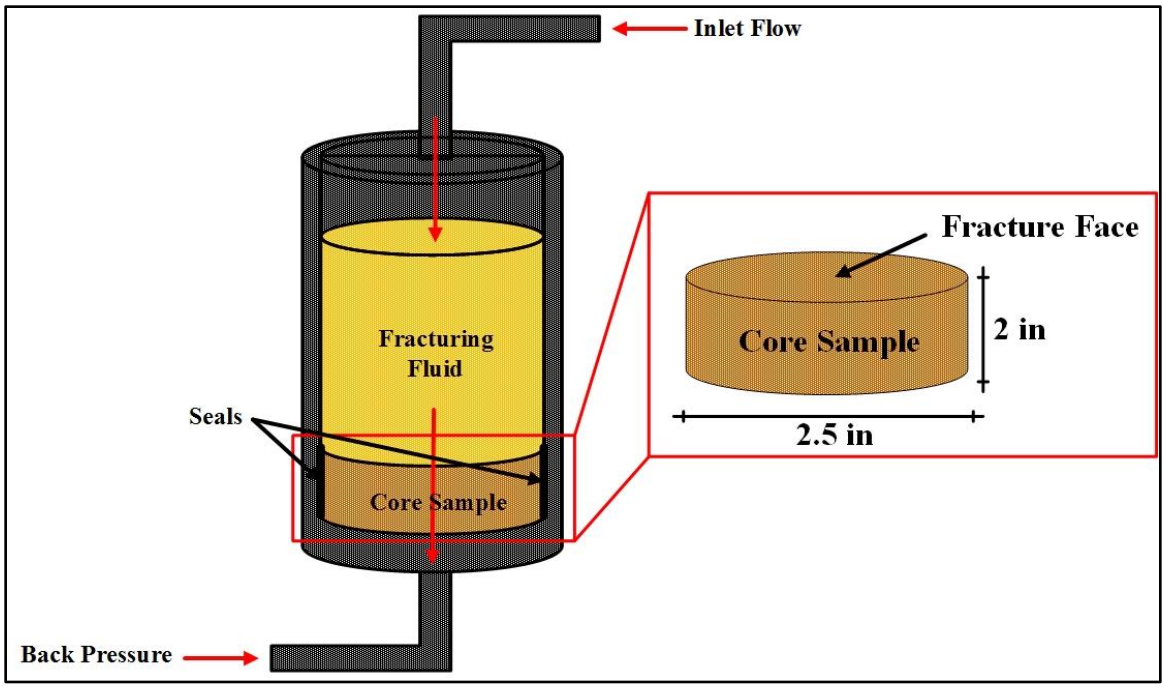

Figure 3.2: Cell and Core specifications of the continuous pumping set up

Filter-Press with continuous pumping steps:

1. Fill the cell from the top with the fracturing fluid, and tighten the cell top and connect the pressure lines coming from the transfer cells.
2. Insert the core sample into the cell and tighten the cell bottom of the cell against the core sample to prevent leaking and attach the pressure lines leading to the back-pressure system.
3. Set the temperature to the required value and allow enough time for the core sample to be heated (about 1 Hour).
4. Apply the required pressure on the transfer cells, and open the valves leading to the core cell, and apply the required back pressure to the system, and open the valves leading to the core cell.

5. Using the water pump, the injection rate was set to the required value and activated to start flooding the core sample, the pressure drop was monitored with time until the required pore volumes were injected. Effluents from some intervals were collected for analysis. The operational parameters of the experiments are shown in Table (3.19 & 3.20).

Table 3.19: Scioto Sandstone core sample continuous pumping operational parameters

Inlet Pressure	500 Psig
Back Pressure	200 Psig
Temperature	300°F
Injection Rate	1 cc/min

Table 3.20:Berea Sandstone core sample continuous pumping operational parameters

Inlet Pressure	500 Psig
Back Pressure	200 Psig
Temperature	300°F
Injection Rate	20 cc/min

3.4 Materials

1. Deionized water.
2. Seawater salts (Sodium Chloride, Calcium Chloride Dehydrate, Magnesium Chloride Hexahydrate, Sodium Sulfate, and Sodium Bicarbonate).
3. KCl salt for brine formulation and NaOH for pH titration.
4. GLDA (Glutamic Acid - Diacetic Acid Chelating Agent) with initial concentration of 40 wt.%.
5. Polymers (AMPS / Co-Polymer, Xanthan, Guar Gum, HPAM and TVP).
6. Sandstone Cores (varying in Permeability from tight to normal).
7. Toluene.
8. NaOH

Figure 3.3: Thermogravimetric Analysis SDT Q600 Instrument

Figure 3.4: FTIR Bruker Tensor27 Instrument

Figure 3.5: Fluid Mixer

Figure 3.6: Weight Balance

Figure 3.7: Grace m5600 Rheometer

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Polymer Stability and Reaction Investigation study using Fresh water and Seawater

4.1.1 Thermogravimetric Analysis (TGA)

Five polymer samples were analyzed using TGA as mentioned in chapter three, the results of the TGA are shown on the following figures (Figures 4.1-4.5). Thermogravimetric analysis showed that HPG polymer had the lowest mass loss of all the tested polymers (11.63%), followed by XC polymer (12.83%), AMPS (13.3%), HPAM (13.8%) and TVP (18.5%). However, the overall tolerance of the five polymers were good when subjected to high temperatures, a 10% average of mass loss of those polymers can be attributed to the residual humidity in the polymer powder and that is indicated by the sharp decline in the mass loss in temperatures up to 212°F, no severe polymer degradation (5%) was noticed in the five polymer samples which indicates that the polymers are resistive when subjected to temperatures similar to reservoir conditions (up to 350°F), and that is evident by the slow slope after 212°F which is the boiling point of water.

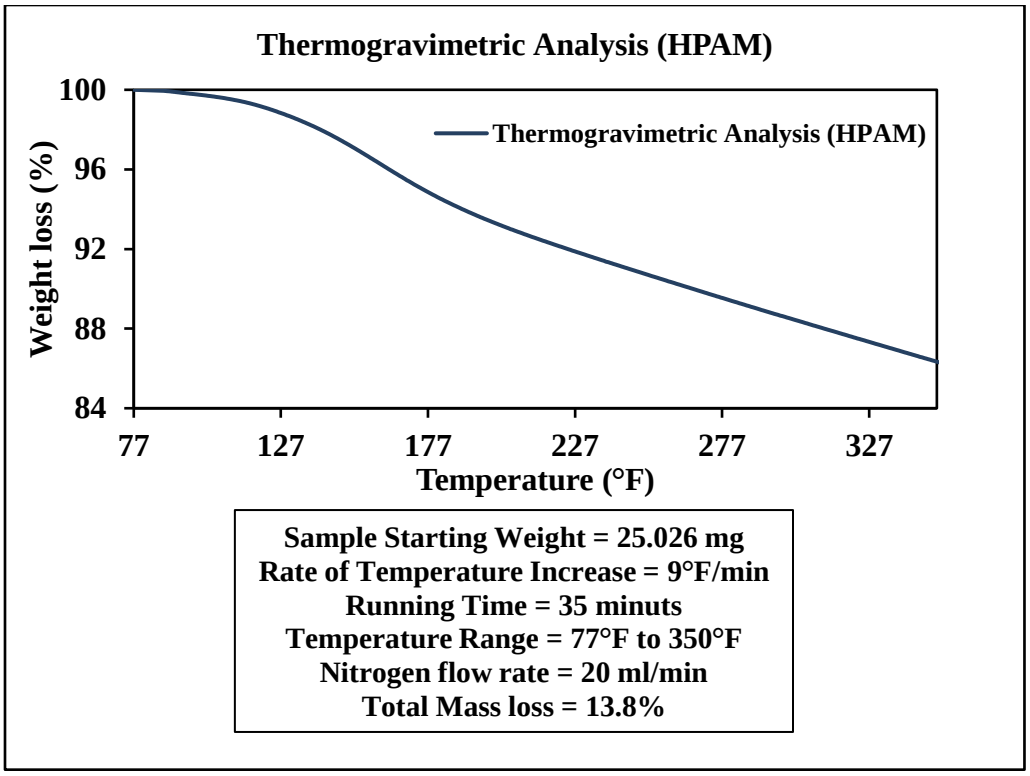

Figure 4.1: Thermogravimetric Analysis (HPAM)

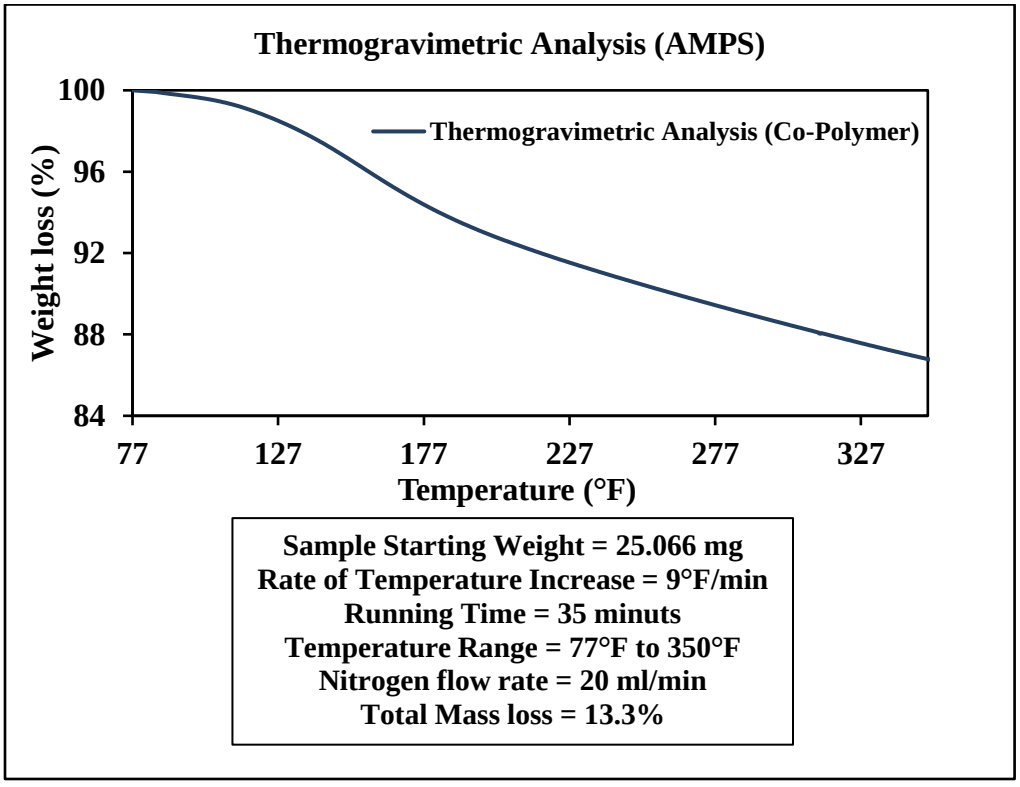

Figure 4.2: Thermogravimetric Analysis (AMPS)

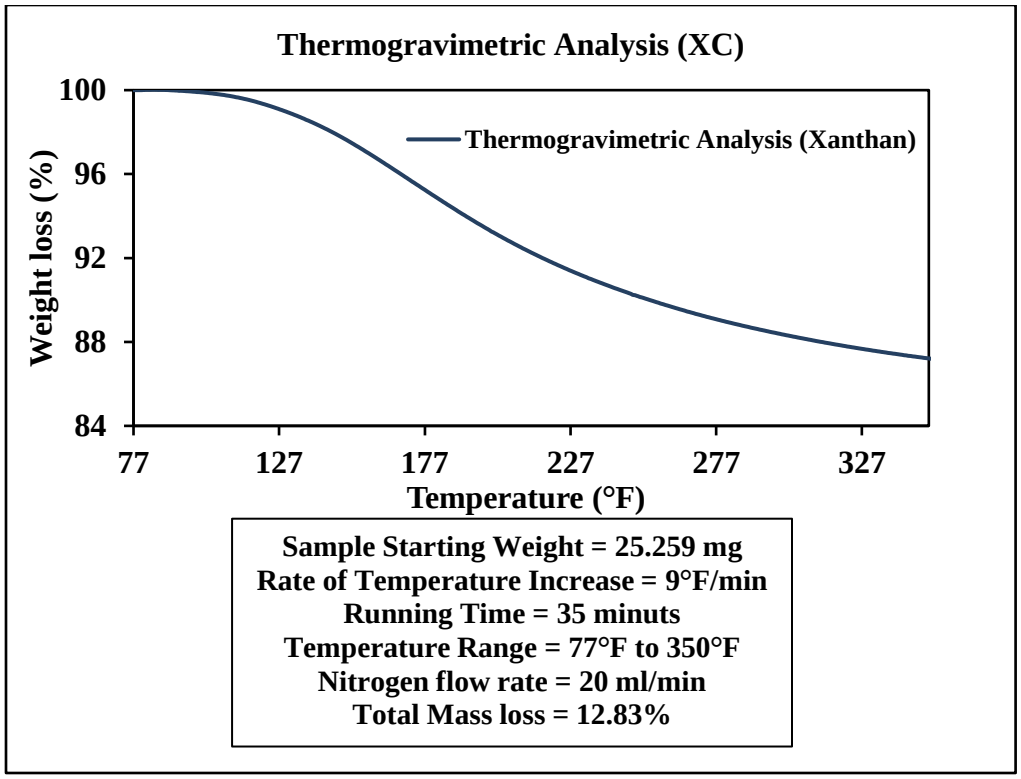

Figure 4.3: Thermogravimetric Analysis (XC)

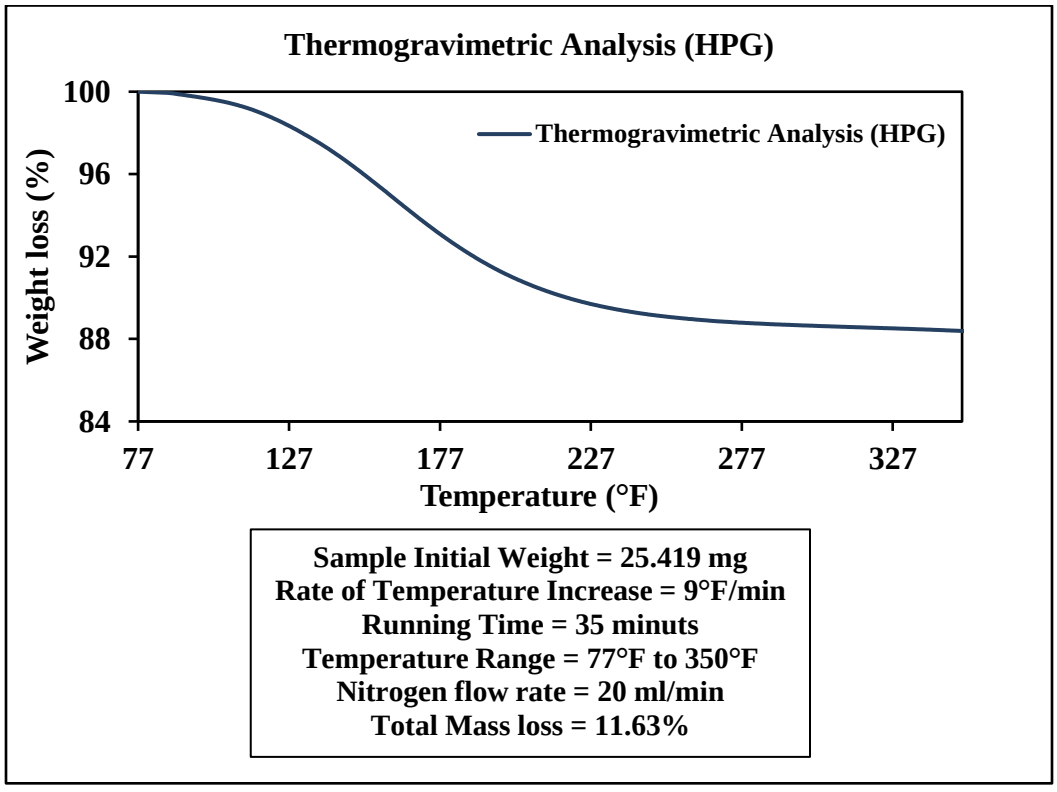

Figure 4.4: Thermogravimetric Analysis (HPG)

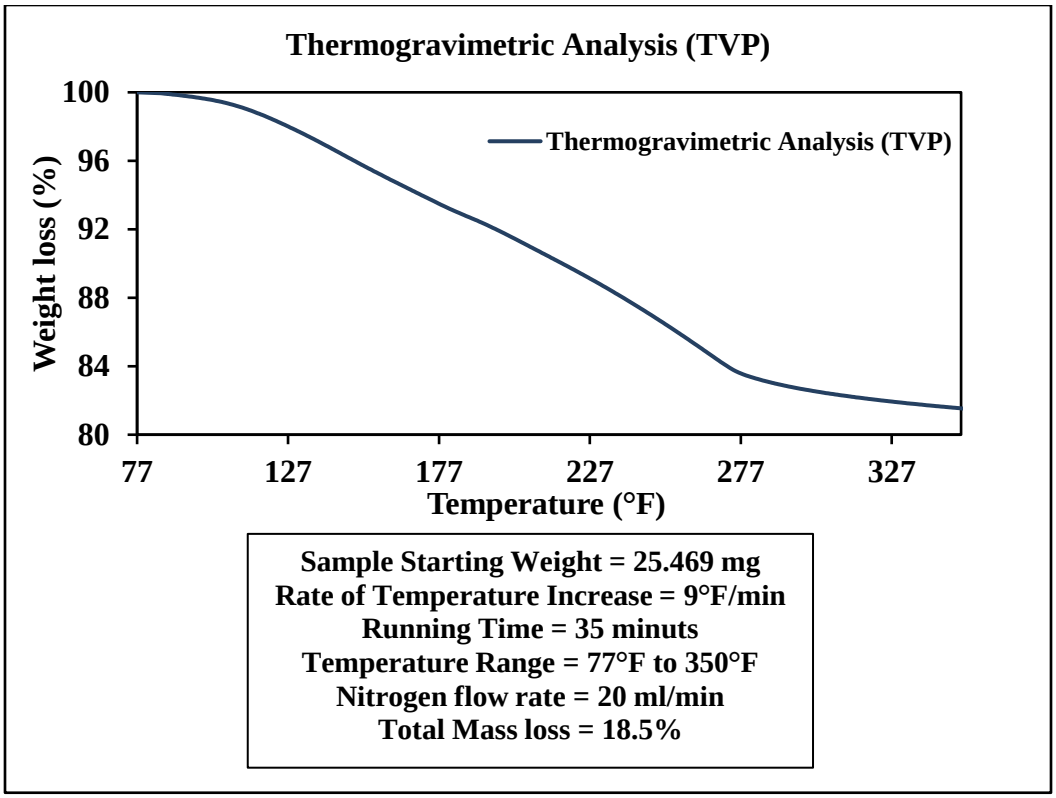

Figure 4.5: Thermogravimetric Analysis (TVP)

4.1.2 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Eight samples (shown in Table 4.1 and Figures 4.6-4.9) which was mentioned in chapter three were prepared for analysis using FTIR analysis, to investigate the mechanism of viscosity thickening and breaking of the developed fluid. The investigation was done on the AMPS as a gelling agent in the developed fluid. The effect of seawater on the fracturing fluid was also investigated. The first four samples were analyzed as base cases for the rest of the samples.

Table 4.1: FTIR experiments list

#	Experiment
1	20 wt.% of GLDA Solution at pH 4
2	20 wt.% of GLDA Solution at pH 12
3	45 pptg of AMPS diluted in DI water
4	45 pptg of AMPS diluted in Seawater
5	20 wt.% of GLDA at pH 12 mixed with 45 pptg of AMPS diluted in DI water (after Thickening)
6	20 wt.% of GLDA at pH 12 mixed with 45 pptg of AMPS diluted in DI water (after Breaking)
7	20 wt.% of GLDA at pH 12 mixed with 45 pptg of AMPS diluted in Seawater (after thickening)
8	20 wt.% of GLDA at pH 12 mixed with 45 pptg of AMPS diluted in Seawater (after Breaking)

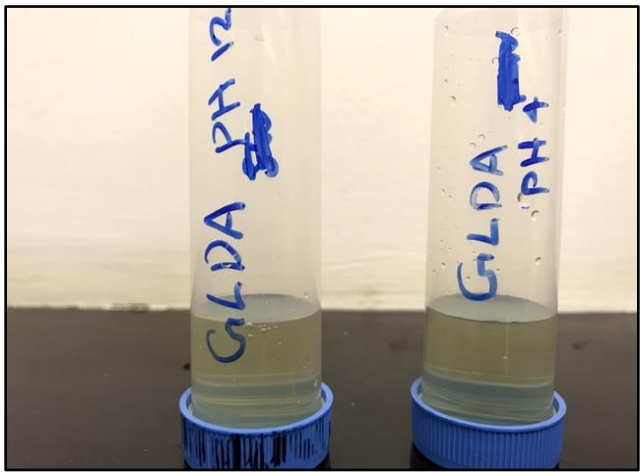

Figure 4.6: GLDA (pH 4 & 12)

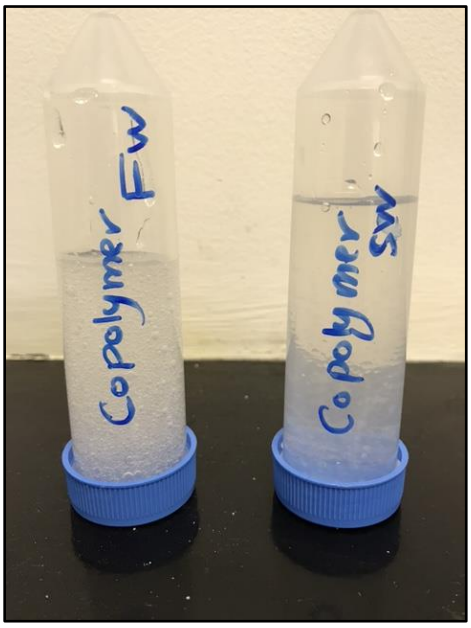

Figure 4.7: AMPS diluted in DI-Water & Seawater

Figure 4.8: The Developed Fracturing Fluid in thickened state (diluted in DI-water and Seawater)

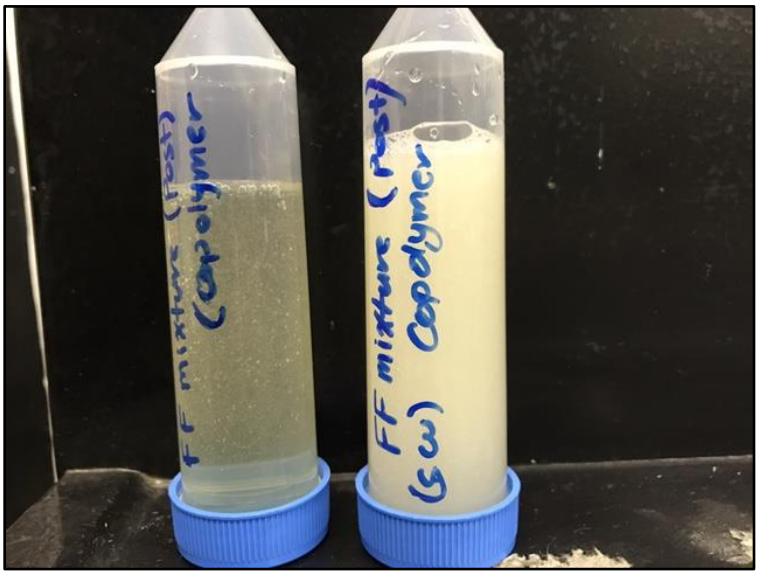

Figure 4.9: The Developed Fracturing Fluid after breaking (diluted in DI-water and Seawater)

Glutamic Acid, N, N-Diacetic (GLDA) has the structure shown on Figure (4.10). FTIR analysis was conducted at pH 4 and pH 12. At pH 4, Figure (4.12), the carboxyl group (C(=O)OH) was identified at the wavenumber 3477 cm^{-1} which is the function group of GLDA, it is characterized by a broad spectrum (at 3477 cm^{-1}) due to the (C=O). The presence of (H-O-) from the carboxyl group was identified at wavenumber 1641 cm^{-1}.

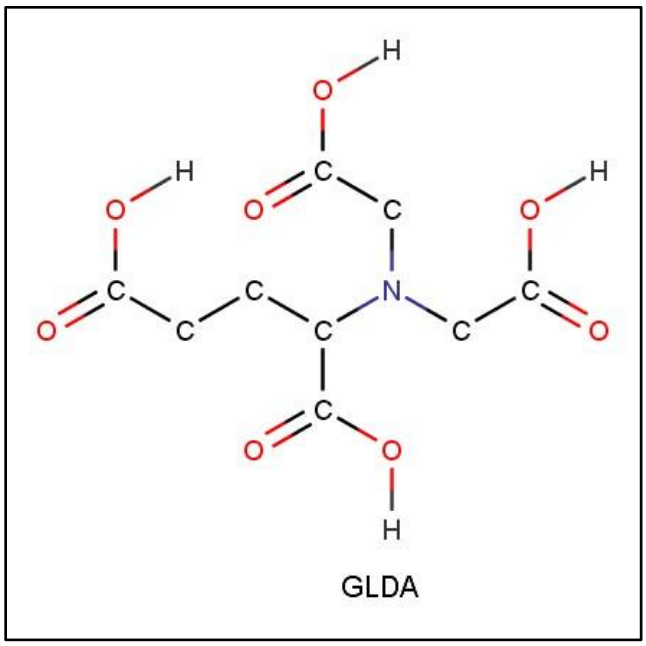

Figure 4.10: GLDA Chemical structure (pH 4)

At the wave number 1396 cm^{-1} a peak was found and it was caused by the (C-N) group, however this group is non-functional group and it will not contribute to thickening and breaking of the polymer.

At pH 12 (shown in Figure 4.13) two peaks were identified at wavenumbers 1587 cm^{-1} and 1685 cm^{-1}, the first was identified as the carboxylate group (COO-) while the later was identified as the carboxyl group (C(=O)OH). The Carbonyl group (C=O) was also identified at wavenumber 3610 cm^{-1}.

Comparing the two spectra at pH 4 and 12, it is clear that increasing the pH of the GLDA frees some of the hydrogen protons and leaves some attached which is evident by the two peaks (at 1587 cm^{-1} & 1685 cm^{-1}). The comparison also shows a slight shift of the carboxyl group due to the proton freeing that occurred. Figure (4.11) shows the chemical structure of GLDA after increasing the pH, and the loss of the H^+ were observed.

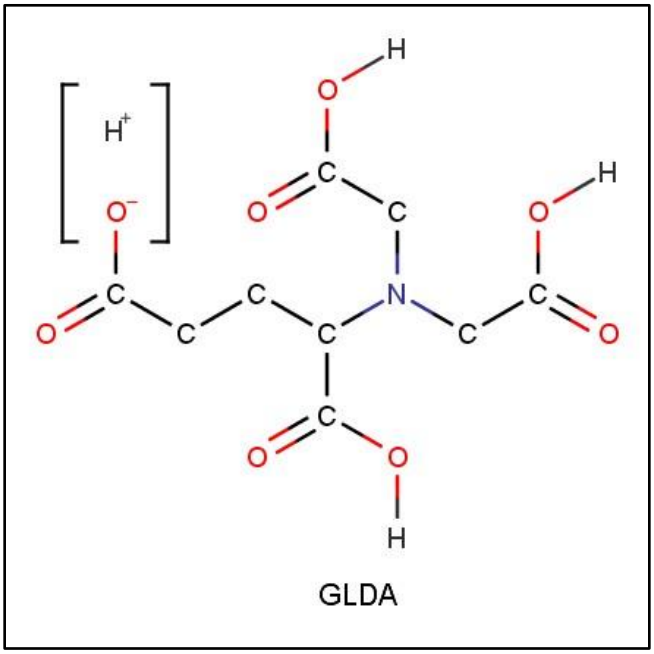

Figure 4.11: GLDA Chemical structure (pH 12)

2-acrylamide-2-methyl propane sulfonic acid (AMPS / Co-polymer) structure is shown in Figure (4.14), FTIR analysis was conducted on this polymer diluted in DI-water. From the spectrum (shown in Figure 4.15), the Acetamide (Amide group) (O=C-NH2) was identified as the functional group in this polymer, with the Carbonyl group (C=O) at a wavenumber 1631 cm^{-1} and (N-H) at wavenumber 3488 cm^{-1}. The broad spectrum at wavenumber 3488 cm^{-1} is also due to the carboxyl group which is present in the polymer.

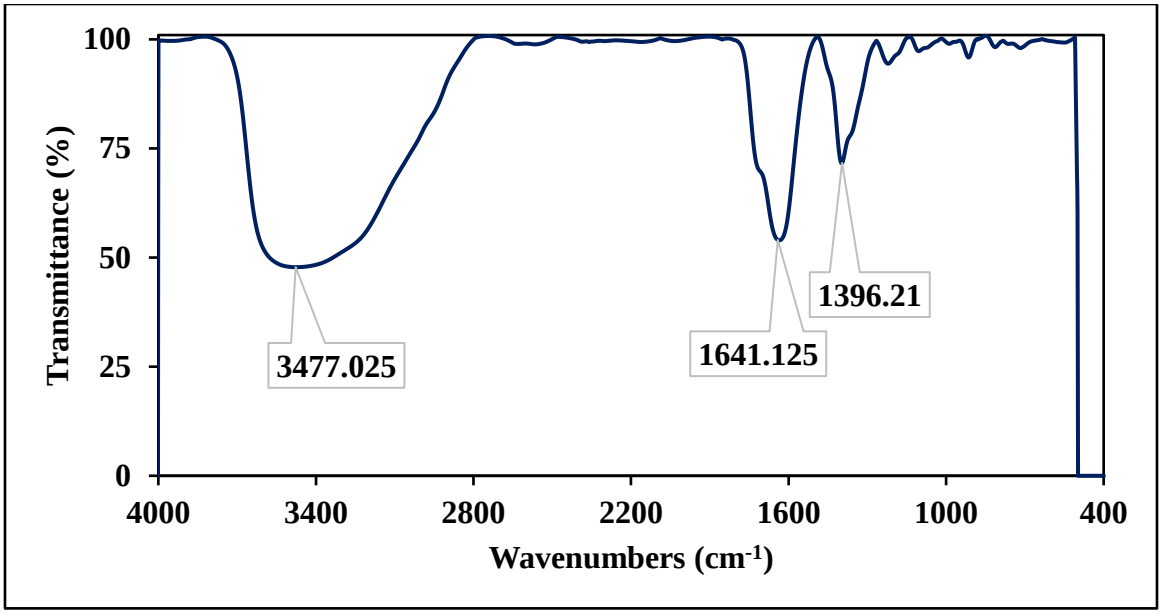

Figure 4.12: FTIR spectrum for GLDA at pH 4

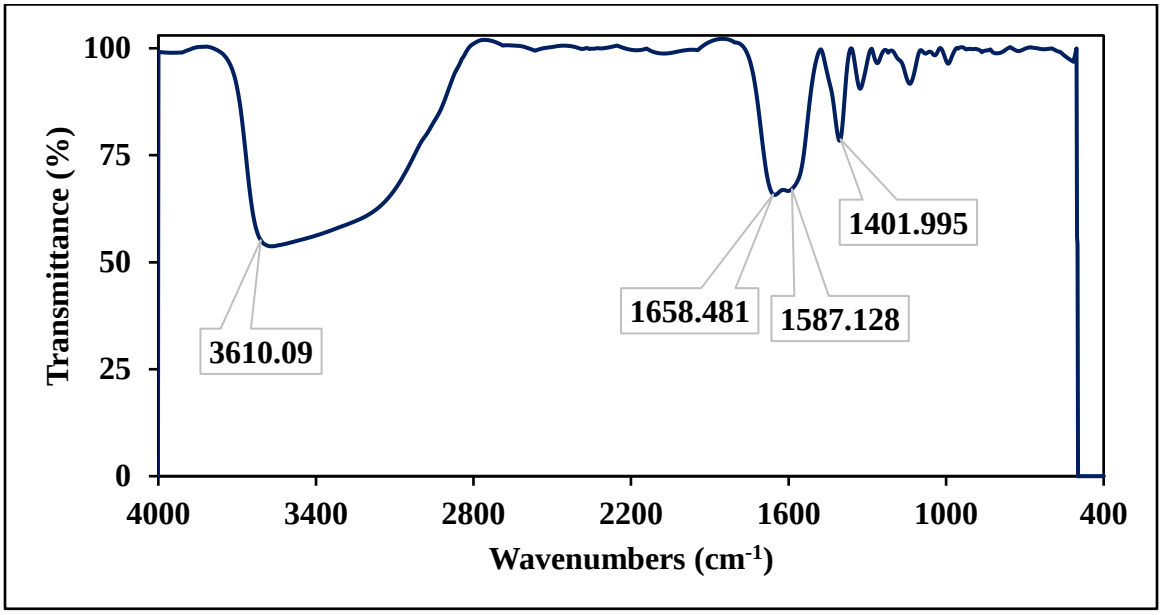

Figure 4.13: FTIR spectrum for GLDA at pH 12

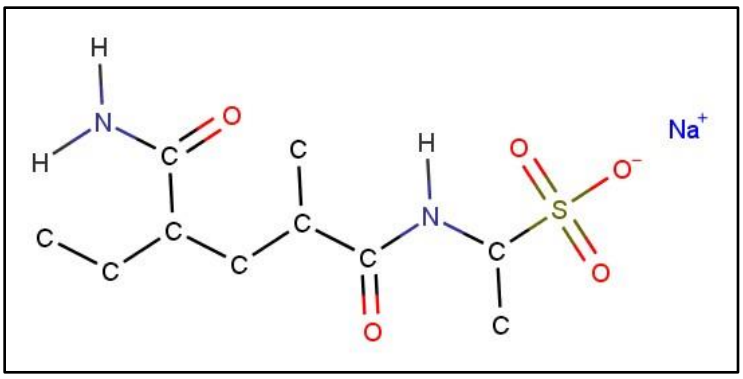

Figure 4.14: 2-acrylamide-2-methyl propane sulfonic acid (AMPS / Co-polymer)

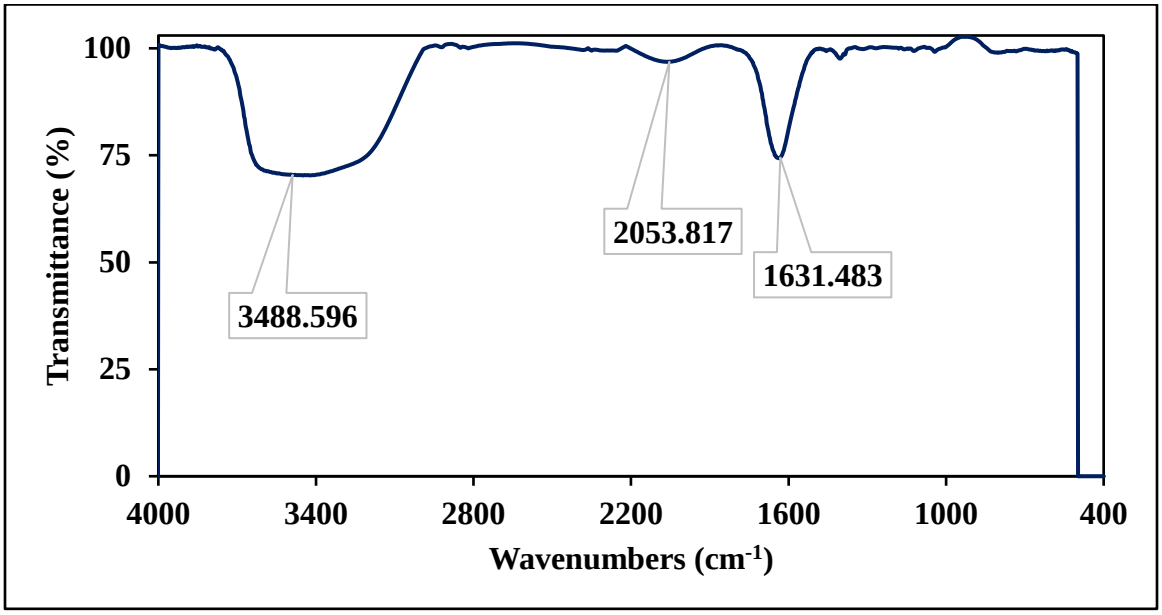

Figure 4.15: FTIR spectrum for AMPS diluted in DI-water

A mixture of GLDA (at pH 12) and AMPS in DI-water was prepared and FTIR analysis was conducted on this fluid at the thickened state (after mixing) and after breakage, to identify the functional groups responsible for the thickening-breaking effect.

From Figure (4.16) the (-O-H) from GLDA appeared at a wavenumber of 3621 cm^{-1} and when compared to Figure (4.15) it shifted by almost 10 cm^{-1} which suggests that the reaction of thickening has occurred and that is due to electrons migration.

At wavenumber of 3158 cm^{-1} the peak was identified as (N-H) from the AMPS, and when compared to Figure (4.15) it experienced high shift due to electron transfer through (C-N) group.

This figure also has two proofs that the reaction took place, the first one is that the carboxamide group (O=C-NH-R) which was in the AMPS was now detected at wavenumber 1563 cm^{-1} which also shifted when compared to Figure (4.15). The second proof is the (O=C-O-R) from the GLDA which is now detected at a wavenumber of 1654 cm^{-1}.

It can be noticed that (C-N) has also shifted from wavenumber 1396 cm^{-1} to 1403 cm^{-1}.

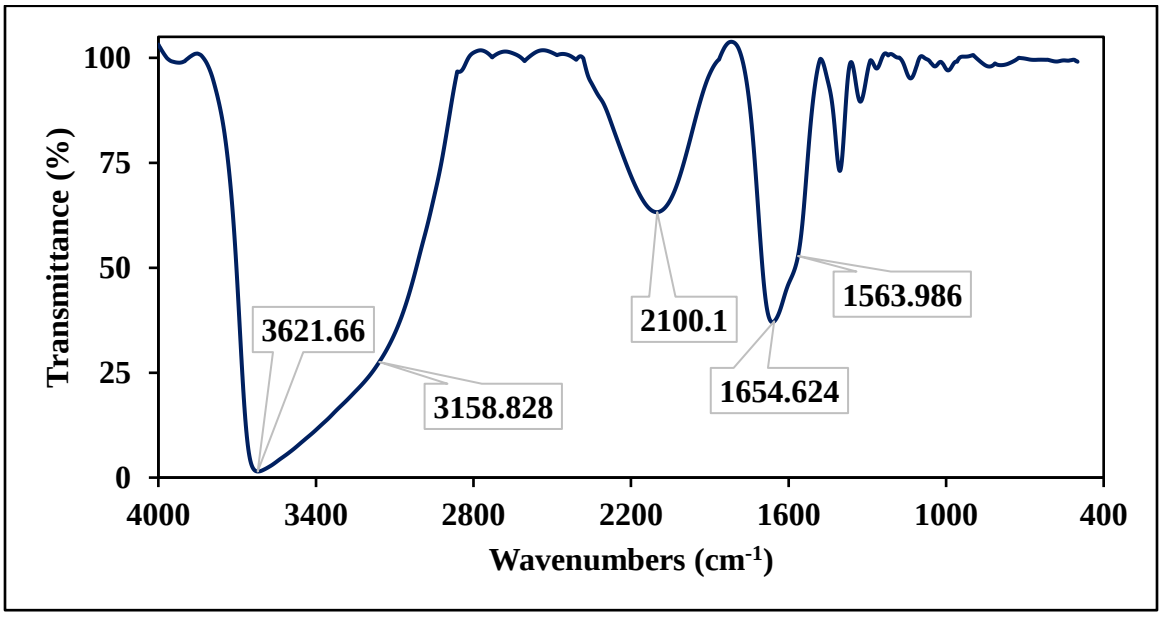

Figure 4.16: FTIR spectrum for the fracturing fluid at thickened state

The mixture's spectrum after breakage is shown in Figure (4.17) the spectrum shows the AMPS amide group at wavenumber of 1560 cm-1 and the GLDA hydroxyl group (O=C-O-H) at wavenumber 1670 cm-1. The spectrum also shows two distinct (C-N) groups peaks forming at wavenumber 1403 cm^{-1} and 1322 cm^{-1}, one coming from the GLDA and the other from the polymer which suggests that the mixture was broken.

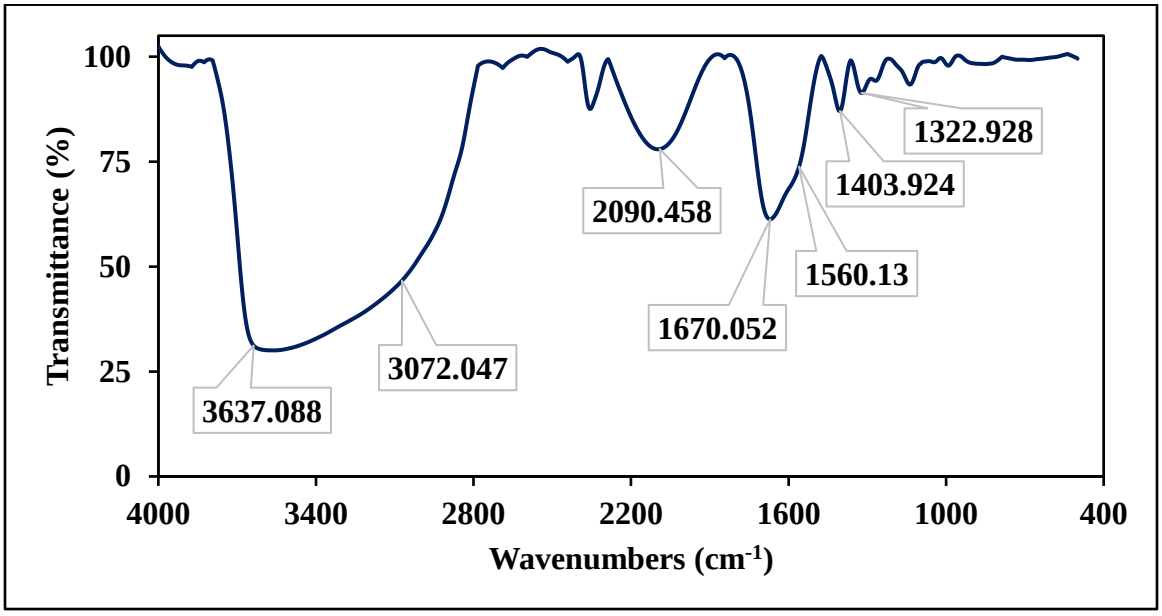

Figure 4.17: FTIR spectrum for the fracturing fluid after break

From Figure (4.17) and the previous analysis the breakage mechanism cause is identified. Some of the (OH-) radicals are still present in the solution from Carboxylic groups originally present in the GLDA. At pH 12 the OH- radicals reacts with the polymer to form water and one polymer radical. The polymer radical then bonds with water again which produces shorter polymer chains and gives off OH- radical again. The OH- radical continues the same sequence and bonds again with polymer and so on, reducing the polymer chains into shorter ones which cause the viscosity drop in the developed fluid.

The increase of temperature activates the reactions and catalyzes the rate of the polymer breakage, which is the reason why the polymer remained stable in room temperatures as it will be seen in the rheology section. However, from the analysis of the previous FTIR spectrums it can be deduced that the thickening and breaking effect of the developed fluid happens simultaneously (in the same time). That is evident by the slight shift of electrons observed, which indicates that there were no major changes of the chemical reactions happen in the duration of the thickening-breaking process of the fluid. Figure (4.18) shows the proposed linkage that happens when the fluid is prepared, (after thickening state).

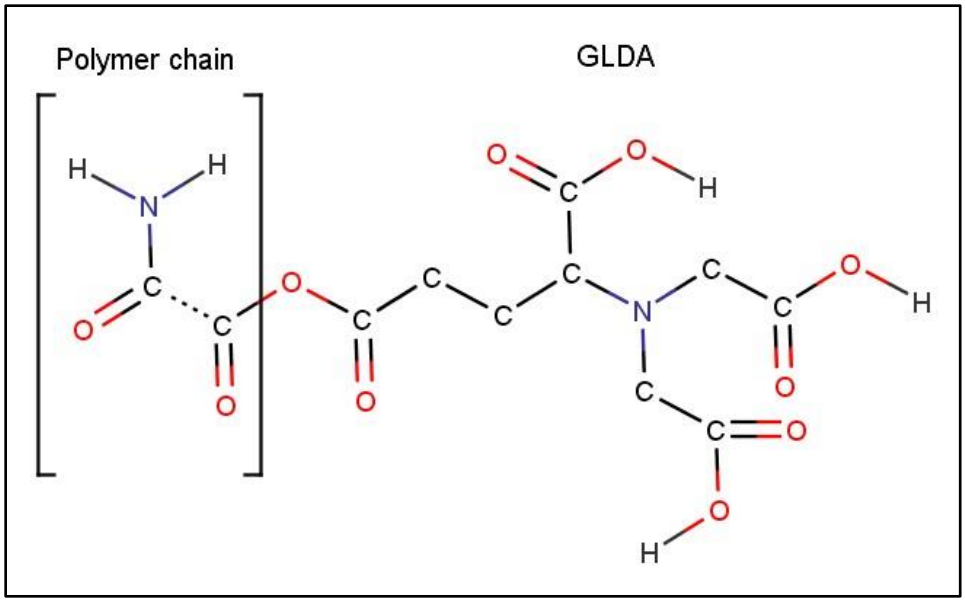

Figure 4.18: Proposed linkage of the developed fluid system (AMPS & GLDA) at pH 12

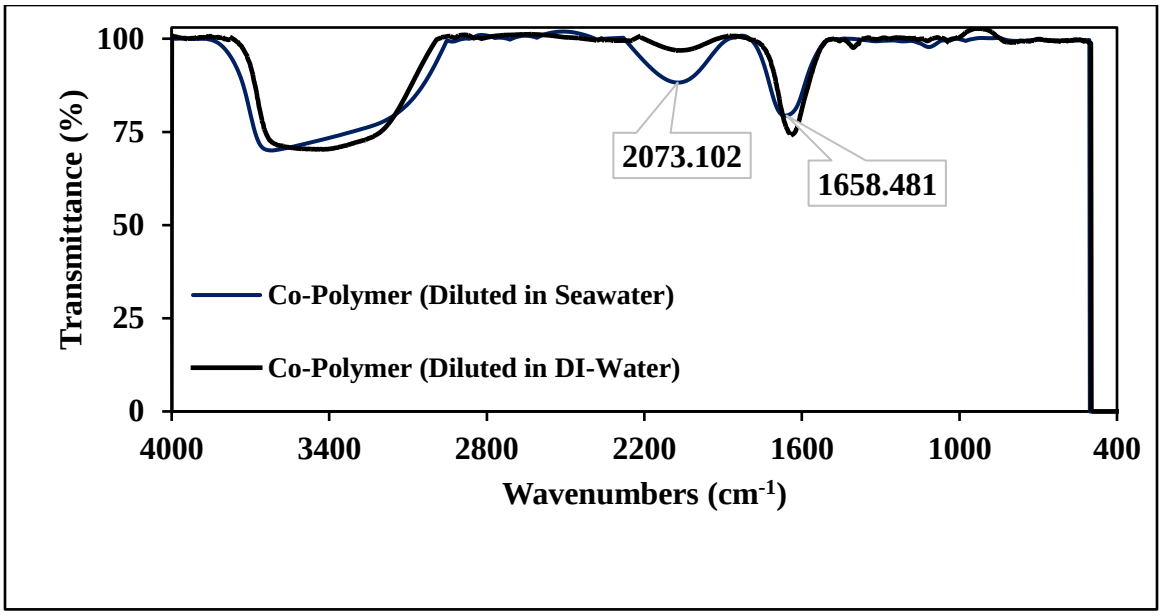

Figure 4.19: FTIR spectrum for AMPS diluted in Seawater

A fracturing fluid was prepared using GLDA mixed with the AMPS in seawater and FTIR analysis was conducted to investigate the reaction occurring when the fracturing fluid is diluted in seawater. Comparing Figures (4.19, 4.20 and 4.21) with Figures (4.15, 4.16 and 4.17) show that the functional groups and reaction taking place in the fracturing fluid is the same, which indicates that seawater is compatible with the developed system. The main difference between the two cases is the stability of the fluid in seawater which decreases due to polymer chains being shrunk by the salt present in the seawater formulation, hence, reducing the viscosity of the fluid. The Figures (4.19-21) also show lower transmittance of the functional groups of the mixture in seawater which supports the previous theory that the salts have an effect of reducing the reaction in fracturing fluid when they are present.

The rheological properties of the mixtures studied here will be determined in the next section.

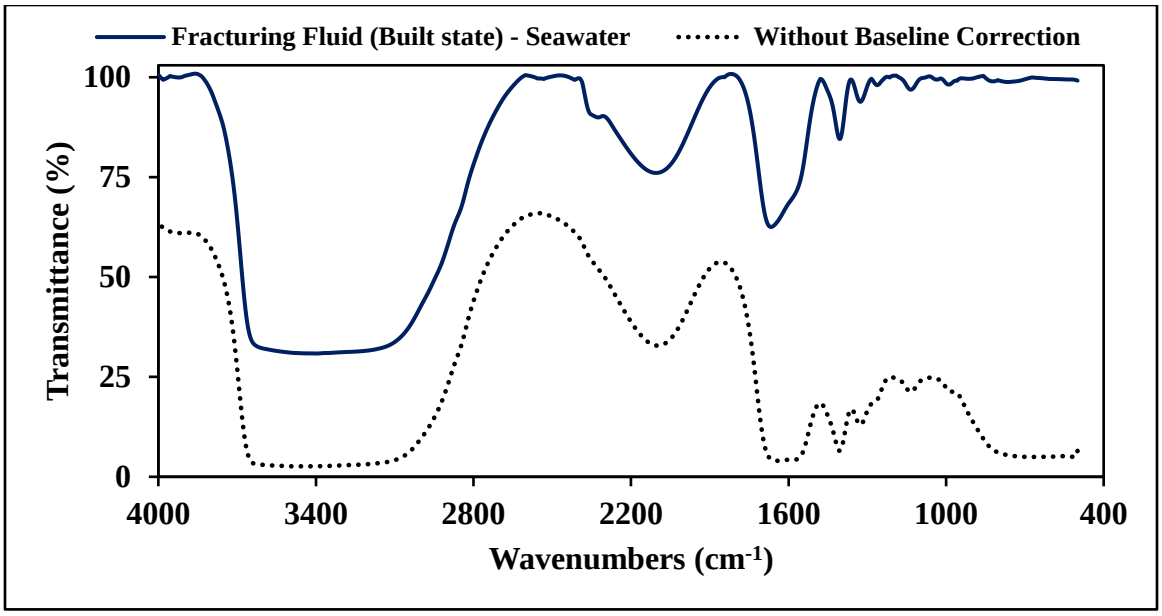

Figure 4.20: FTIR spectrum for the developed fluid diluted in Seawater (thickened state)

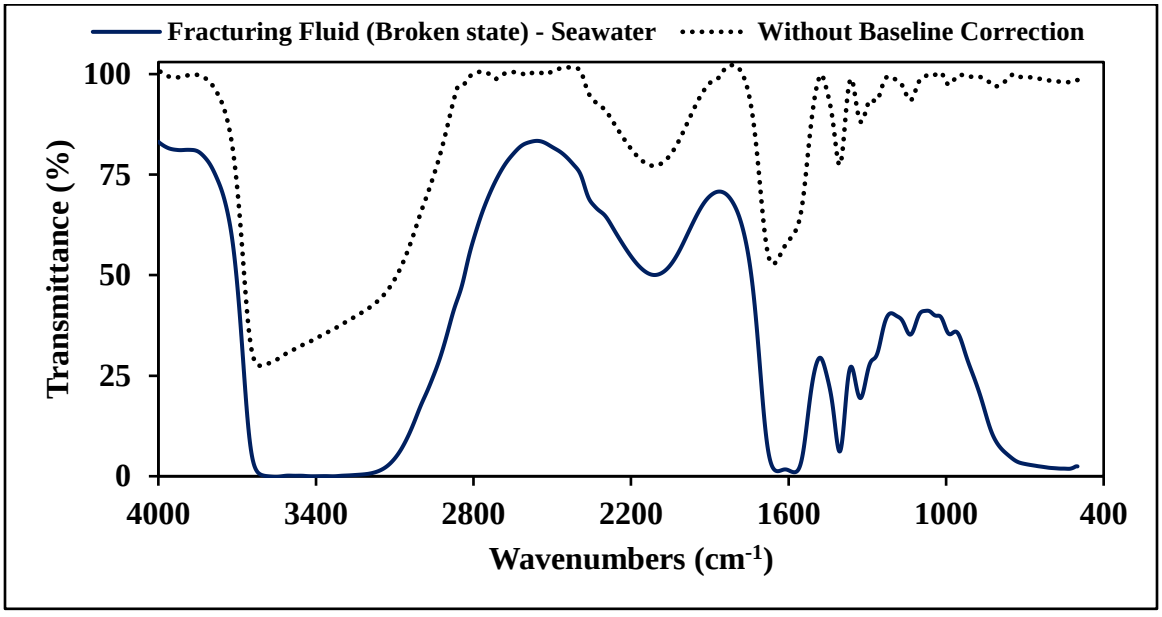

Figure 4.21: FTIR spectrum for the developed fluid diluted in Seawater (after break)

4.2 Development of the Fracturing Fluid Using Fresh Water

4.2.1 Polymer and Chelating agents screening

Three experiments were conducted to determine the effectiveness of several chelating agents with the polymers in terms of the thickening-breaking efficiency. 20 wt.% of DTPA, GLDA, and EDTA were evaluated against XC polymer at a concentration of 0.43 wt.%, a shear rate of 170.3s^{-1} and temperature of 200°F.

Figure (4.22) shows the results of the experiments, DTPA, GLDA, and EDTA exhibited a thickening effect, however only GLDA experienced breaking behavior without the addition of breakers. From this DTPA and EDTA were excluded from further testing. It is, however, worth mentioning that the other two chelating agents can be used if a breaker is to be introduced to the system.

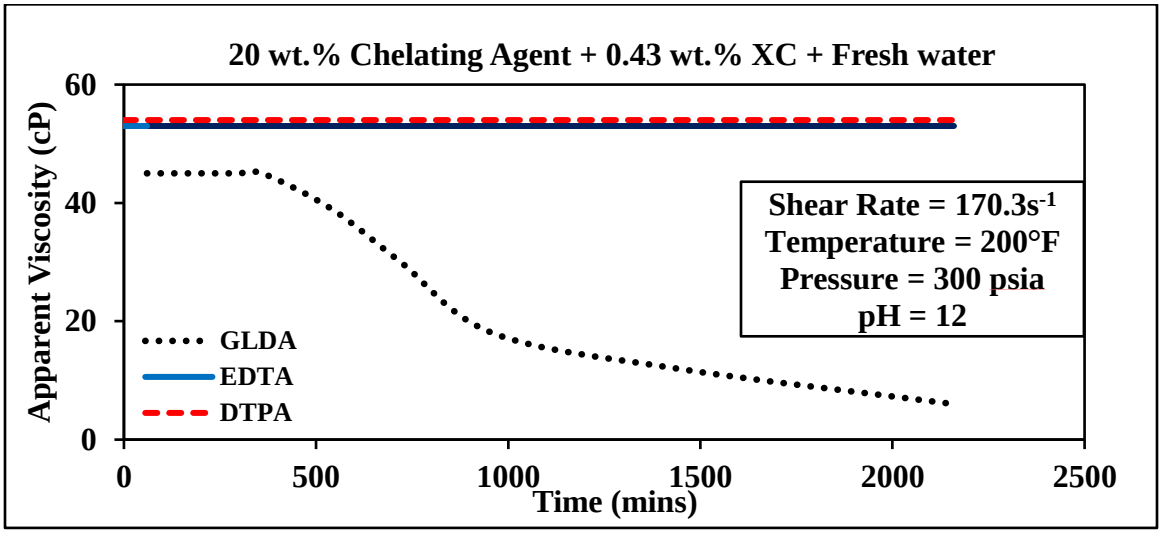

Figure 4.22: Chelating agents screening experiments' results

20 wt.% of GLDA and 20 pptg of several polymers (TVP, HPG, XC and HPAM) were mixed and the apparent viscosity was measured versus mixing time for each sample, the

pH of the mixture was fixed at pH 12 and the shear rate was 511s^{-1}. The experiment was conducted at 300°F.

As indicated in Figure (4.23) the viscosity of the XC polymer had the best thickened viscosity compared to the other polymers, followed by HPAM, the polymers exhibited uniform stability regardless of the thickened viscosity.

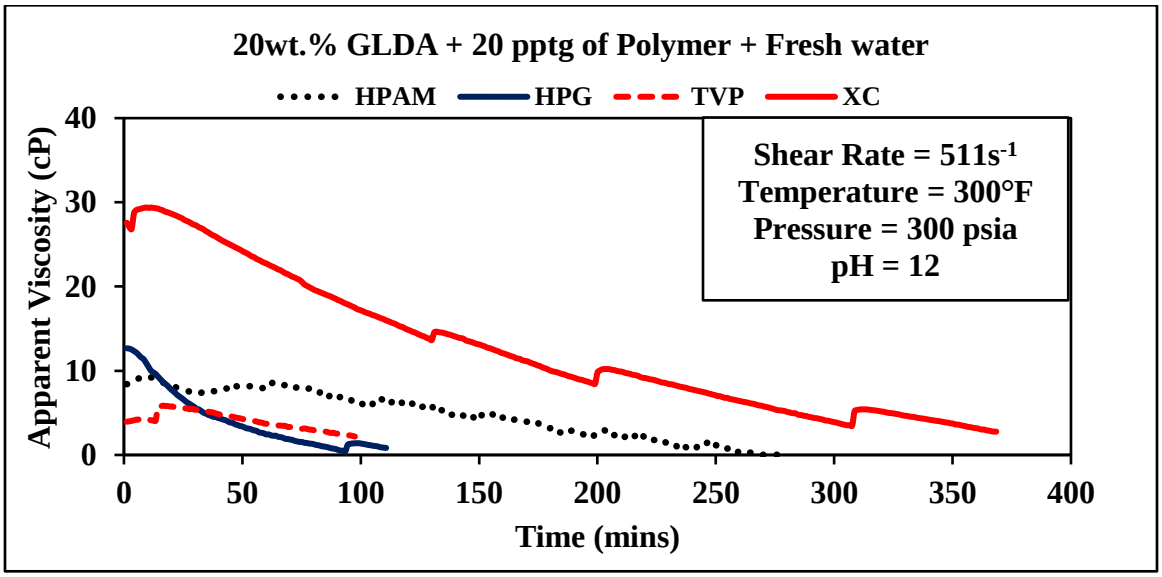

Figure 4.23: Viscosity profile of multiple polymers with GLDA

4.2.2 The effect of pH on the fracturing fluid behavior

20 wt.% of DTPA (Diethylenetriaminepentaacetic Acid chelating agent) and 0.43 wt.% of Xanthan polymer (XC) were mixed, the apparent viscosity was measured versus time, the temperature was fixed at 200°F and the shear rate was 170.3s^{-1}. The experiments were conducted at pH 4, 7 and 12.

The results of these experiments showed that mixing DTPA with XC increased the apparent viscosity from 33 cP (the apparent Viscosity of 0.43 wt.% XC alone) to 55 cP in each pH value. This indicates a successful viscosity thickening effect on the solution

between the branched molecules of the polymer using DTPA at different pH values (Acidic, Alkaline and Neutral). However, the viscosity of this mixture remained constant throughout the experiment and no breakage behavior was observed, the results of the experiment are shown in Figure (4.24).

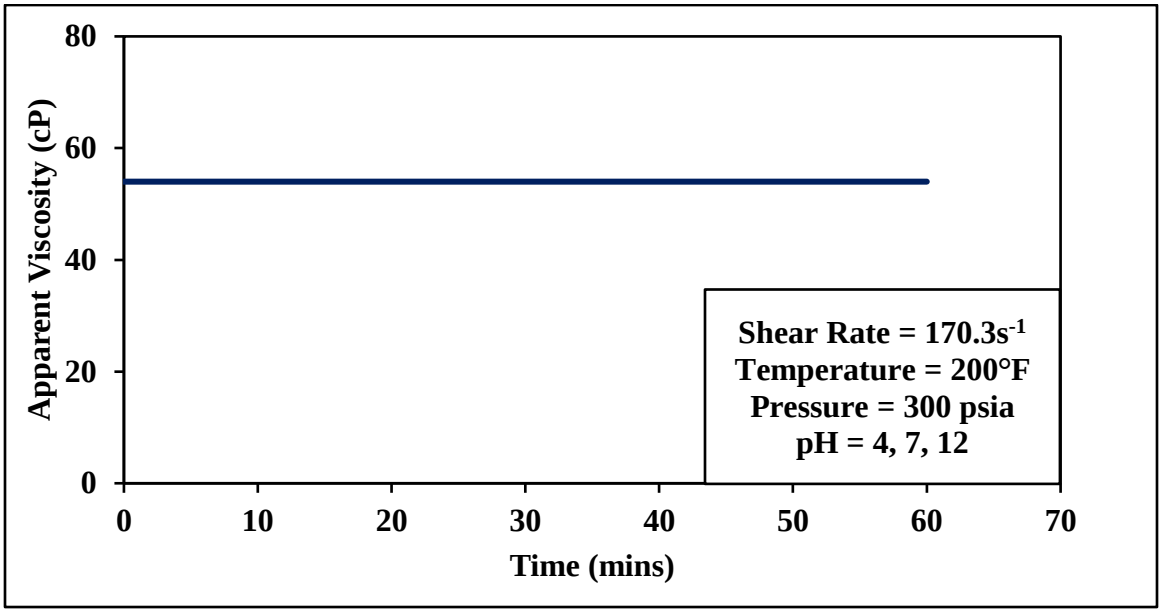

Figure 4.24: Viscosity measurements of 20 wt.% DTPA with 0.43 wt.% XC with time at different pH values

20 wt.% EDTA (Ethylenediaminetetraacetic chelating agent) and 0.43 wt.% Xanthan polymer (XC) were mixed. The apparent viscosity was measured versus mixing time, the temperature was fixed at 200°F and the shear rate was $170.3s^{-1}$. The experiment was conducted at pH 7 and 12.

The results of this experiment showed that mixing EDTA with XC also increased the apparent viscosity from 33 cP (the apparent Viscosity of 0.43 wt.% XC alone) to 42 cP for the pH value of 7, and 55 cP for the pH value of 12. This indicates a successful thickening of the solution using EDTA at different pH values (Alkaline and Neutral),

however, the viscosity of this mixture remained constant throughout the experiment and no breakage behavior was observed, the results of the experiment are shown in Figure (4.25).

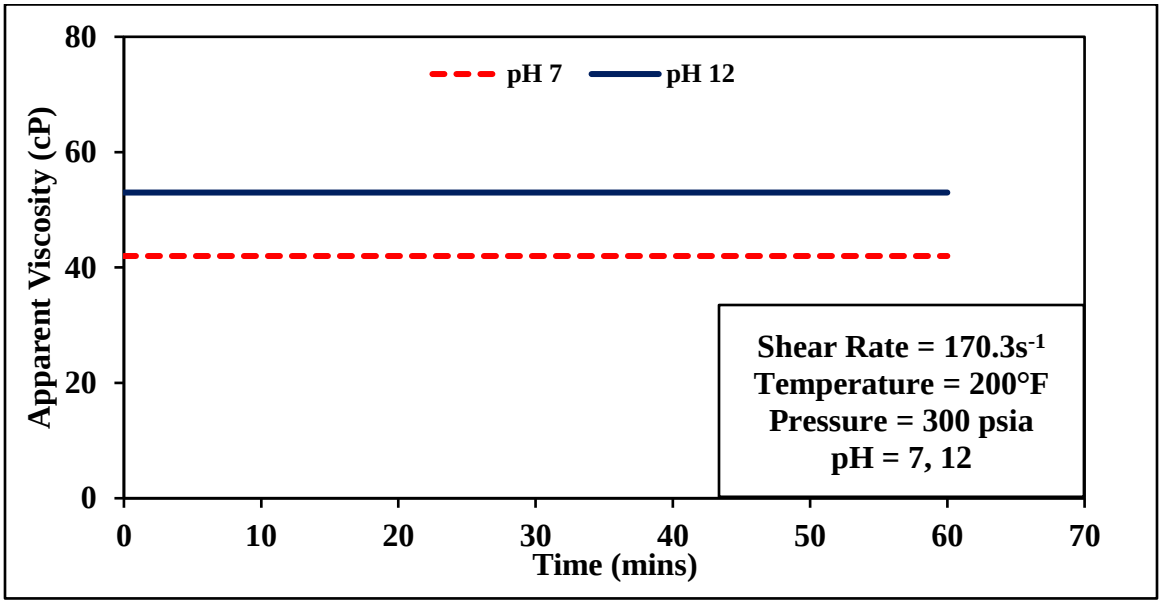

Figure 4.25: Viscosity measurements of 20 wt.% EDTA with 0.43 wt.% XC with time at different pH values

20 wt.% GLDA (Glutamic Acid, N, N-Diacetic Acid, the chelating agent used in this study) and 0.43 wt.% Xanthan polymer (XC) were mixed. The apparent viscosity was measured versus mixing time, the temperature was fixed at 200°F and the shear rate was $170.3s^{-1}$. The experiment was conducted at pH 4, 7, and 12.

The results of this experiment showed that mixing GLDA with XC also increased the apparent viscosity from 33 cP (the apparent Viscosity of 0.43 wt.% XC alone) to 55 cP for the pH value of 4 and after 10 hrs of mixing. Some of the linked branches of the polymer were broken, hence reducing the apparent viscosity of the mixture to 50 cP, at pH 7 the viscosity increased to 75 cP, and after 3.5 hrs of mixing. Small amounts of the

linked branches were broken reducing the apparent viscosity to 60 cP, at pH 12, thickening was successful, and the apparent viscosity of the mixture increased to 45 cP. After 7 hrs of mixing the polymer branches were broken, and the polymer backbone (main structure of the polymer) as well, hence reducing the viscosity below the initial value of the XC polymer alone. This indicates breaking characteristics of GLDA at pH 12. The results of the experiment are shown in Figure (4.26).

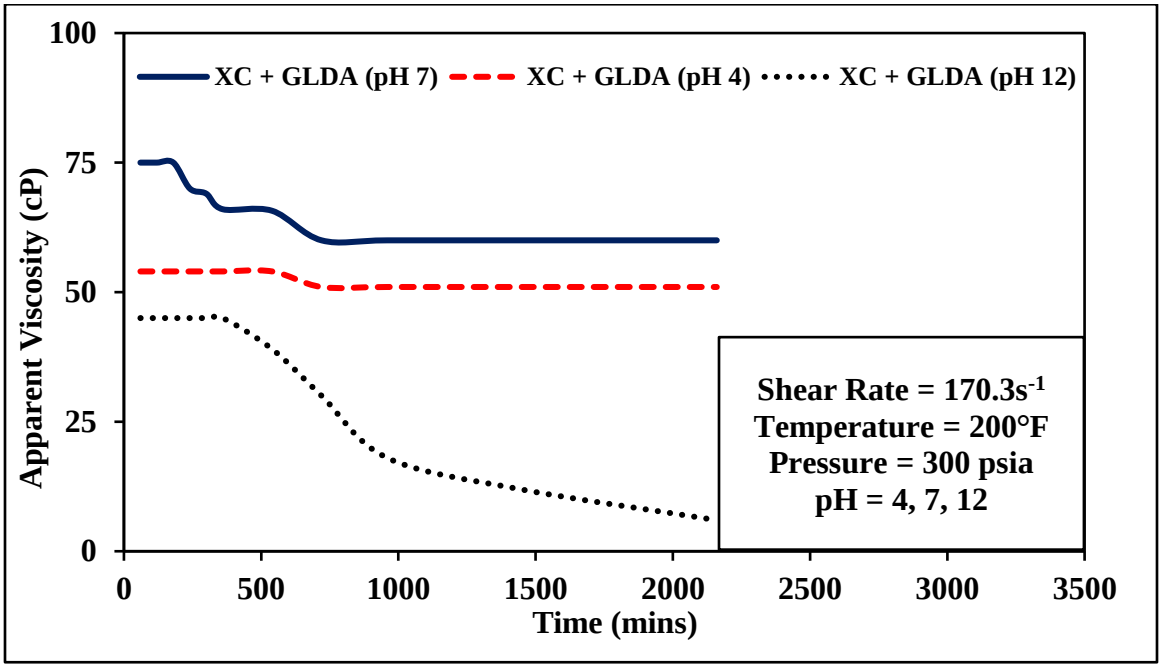

Figure 4.26: Viscosity measurements of 20 wt.% GLDA with 0.43 wt.% XC with time at different pH values

20 wt.% of GLDA and 20 pptg of AMPS were mixed, the apparent viscosity was measured against mixing time, the temperature was fixed at 200°F and the shear rate was $511s^{-1}$. The experiments were conducted at pH 4 and 7.

The results of this experiment showed that mixing GLDA with the AMPS increased the viscosity from the basic viscosity of the polymer solution alone, and remained constant

throughout the experiment, however at pH 7 the increase in viscosity was greater than at pH 7 at the same conditions and at pH 12 the viscosity was even higher than both pH 4 and 7 which indicates that the viscosity increases with the increase of pH when using AMPS. However, no breakage of the solution's viscosity was observed on both pH 4 and 7 cases. The results of the experiments are shown in Figure (4.27).

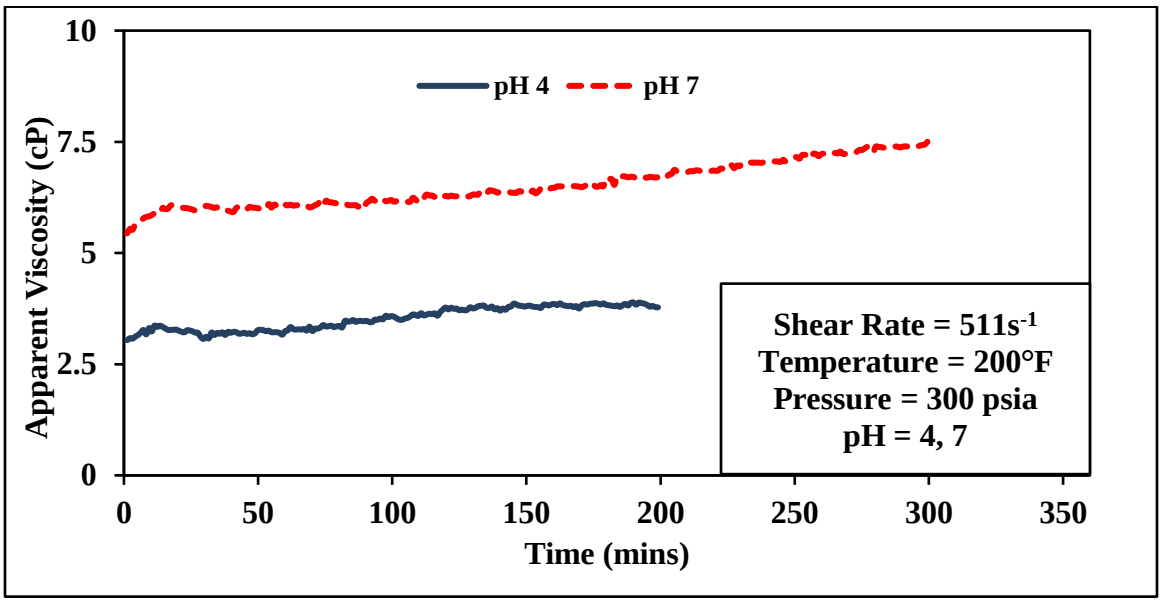

Figure 4.27: Viscosity measurements of 20 wt.% GLDA with 20 pptg of AMPS with time at different pH values

4.2.3 The effect of Temperature on the fracturing fluid behavior

20 wt.% of GLDA and 0.43 wt.% of Xanthan polymer (XC) were mixed and the apparent viscosity was measured against mixing time, the pH of the mixture was fixed at pH 12 and the shear rate was 170.3s^{-1}. The experiment was conducted with varying temperatures (at room temperature 77°F and 200°F).

As shown from the previous experiment, the viscosity of the mixture increased from 33 cP (the apparent viscosity of 0.43 wt.% XC alone) to 45 cP and then broke after 7 hrs of mixing to an apparent viscosity value below the initial value, the experiment was

conducted at 200°F. another similar experiment was conducted at room temperature, the results showed that the apparent viscosity increased to a value of 50 cP and remained intact throughout the entire time of mixing (approx. 40 hrs), which indicated failure of breaking at room temperature. The results are shown in Figure (4.28).

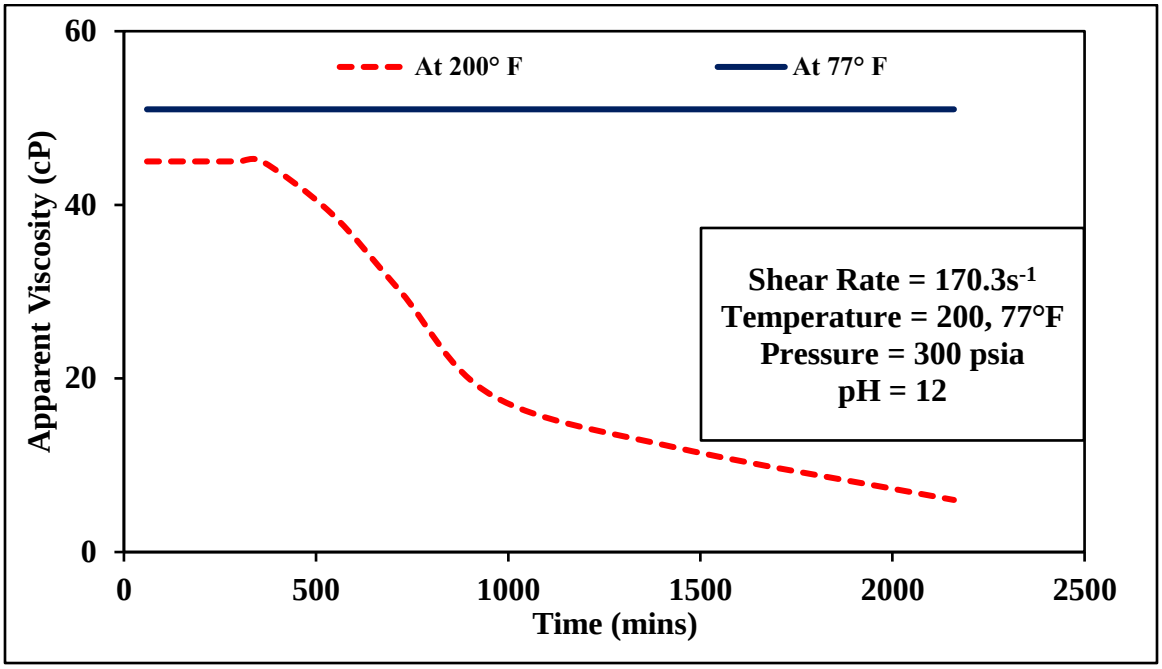

Figure 4.28: Viscosity measurements of 20 wt.% GLDA with 0.43 wt.% XC with time at temperatures

20 wt.% of GLDA and 20 pptg of AMPS were mixed and the apparent viscosity was measured versus mixing time, the pH of the mixture was fixed at pH 12 and the shear rate was $511s^{-1}$. The experiment was conducted at 77°F.

As indicated in Figure (4.29) the viscosity of the fluid remained constant throughout the experiment time, and no breakage behavior was noticed. This indicates that at room temperature the GLDA thickens the polymer solution but it does not break it.

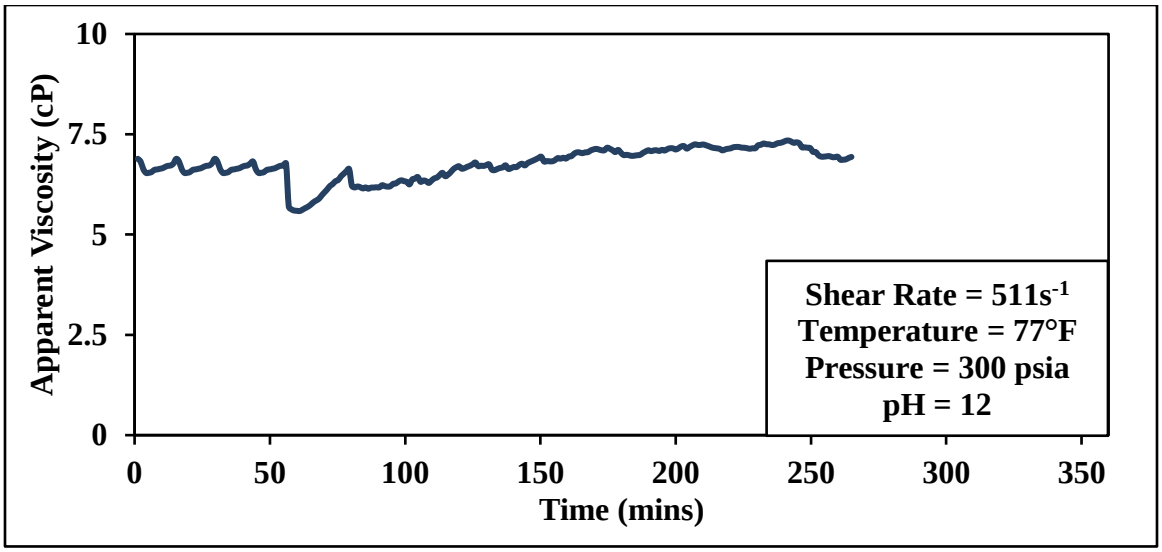

Figure 4.29: Viscosity measurements of 20 wt.% GLDA with 20 pptg of AMPS with time at room temperature

4.2.4 The effect of Polymer type and concentration on the fracturing fluid behavior

Two polymers were tested against the GLDA which included (XC and a AMPS), on the following experiment 20 wt.% of GLDA and 0.43 wt.% of Guar Gum were mixed and the apparent viscosity was measured, the shear rate was fixed at 170.3s^{-1}. The experiment was conducted at pH 4, and at temperature of 200°F, the goal of this experiment was to check whether other polymers exhibits the same thickening-breaking behavior after mixing with GLDA.

The results of this experiment showed that mixing GLDA with Guar gum at 200°F increased the apparent viscosity from 33 cP (the apparent Viscosity of 0.43 wt.% Guar Gum alone) to 70 cP for the pH value of 4, and after 24 hrs of mixing, the apparent viscosity also declined to a value of 4 cP which is below the initial apparent viscosity of Guar Gum alone, indicating the breakage of the polymer main structure and the linked branches. The experiment showed that GLDA mixed with Guar Gum has thickening

abilities and breaking at pH 4 and at 200°F. the results of the experiment is shown in Figure (4.30).

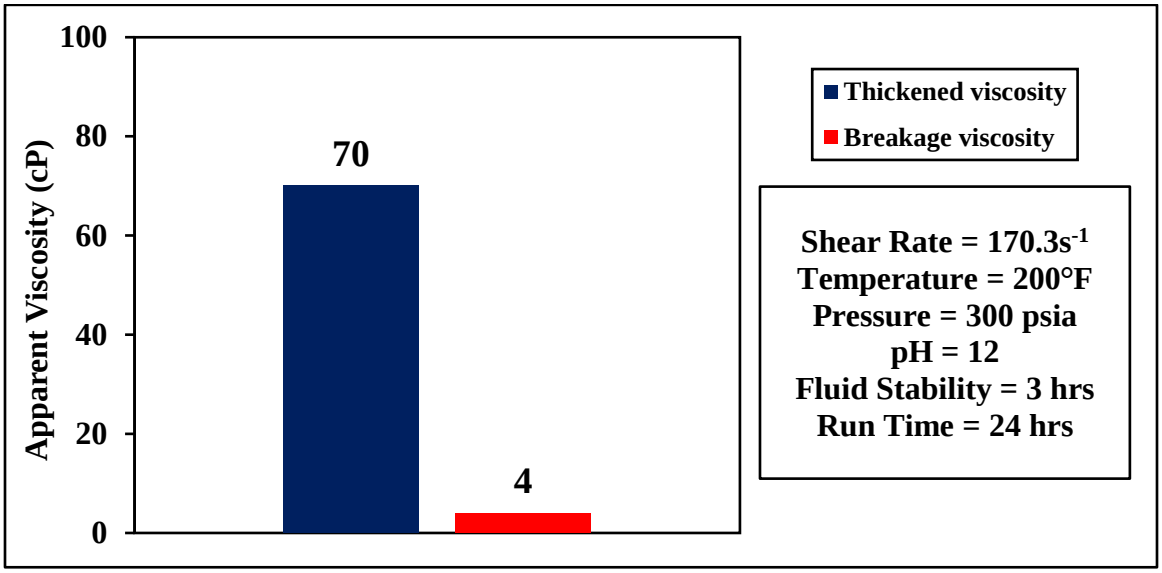

Figure 4.30: Viscosity measurements of 20 wt.% GLDA with 0.43 wt.% Guar Gum at the beginning of the mixing and after 24 hrs of mixing

20 wt.% of GLDA were mixed with 20 and 70 pptg of AMPS and the apparent viscosity was measured against mixing time, the pH of the mixture was fixed at pH 12 and the shear rate was $511s^{-1}$. The experiment was conducted at 200°F.

As shown in Figure (4.31), the experiment conducted using 20 pptg of AMPS the viscosity was built after almost 50 minutes after mixing and remained stable for 50 minutes until it started to break gradually, however when the polymer concentration was increased to 70 pptg the viscosity also built after 40 minutes but declined sharply after 20 minutes which indicates breaking of the polymer chains. We can conclude that with the increase of polymer concentration the viscosity of the thickened fluid increases also but the stability of the fluid with time under constant shearing decreases.

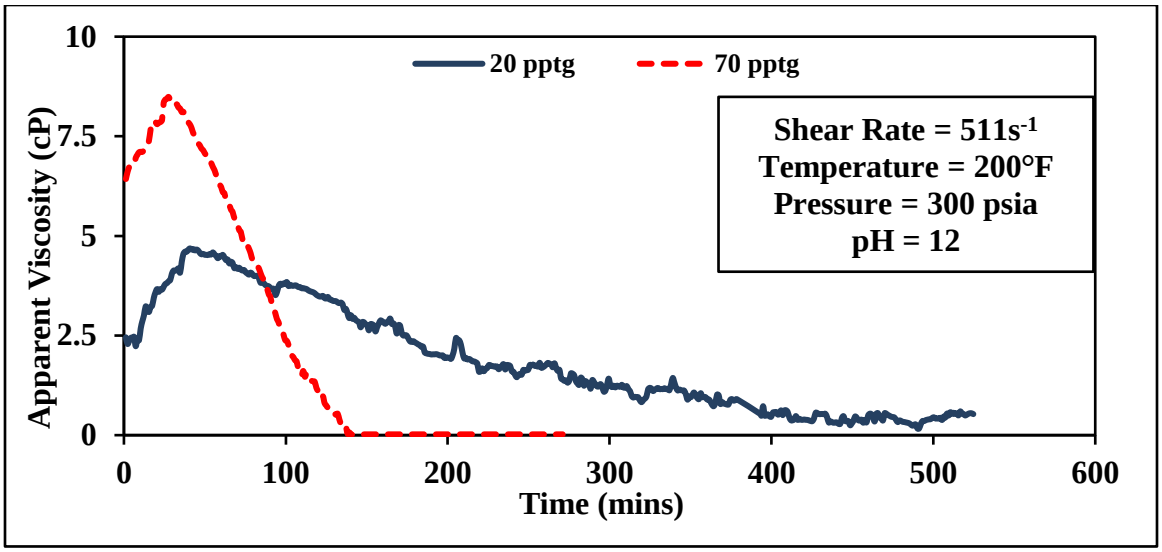

Figure 4.31: Viscosity measurements of 20 wt.% GLDA with 20 pptg of AMPS at different concentrations

4.2.5 The effect of GLDA (Diluted in DI-water) concentration on the fracturing fluid behavior

Five experiments were conducted by mixing 45 pptg of AMPS with 5, 10, 20, 30, 40 wt.% of GLDA, the apparent viscosity was measured with running time, the pH of the GLDA was fixed at 12, the shear rate at $511s^{-1}$, and the temperature at 300°F.

As observed from Figures (4.29-4.38) 5 wt.% of GLDA yielded a very stable solution under high temperature high pressure conditions but the viscosity increase was minimal due to the small concentration of GLDA. The solution's viscosity is very close to the viscosity of the polymer alone, which indicates that the thickening effect was also minimal on this solution. Breakage occurred in a gradual manner also due to the same reason. Increasing the concentration to 10, 20 or 30 wt.% of GLDA increased the thickening effect on the solution but reduced the stability of the fluid, however the viscosity increase was large which indicates a successful thickening of the fluid. Breakage of this fluid however was sharp compared to the 5 wt.% case, using a 40 wt.%

concentration of GLDA yielded the same behavior of the fluid but the thickening effect was reduced evident from the viscosity of the fluid which was less than the 20 wt.% and 30 wt.%, which indicates that the viscosity thickening effect can be controlled with the concentration of GLDA, and for optimum conditions it should not be more than 30 wt.%.

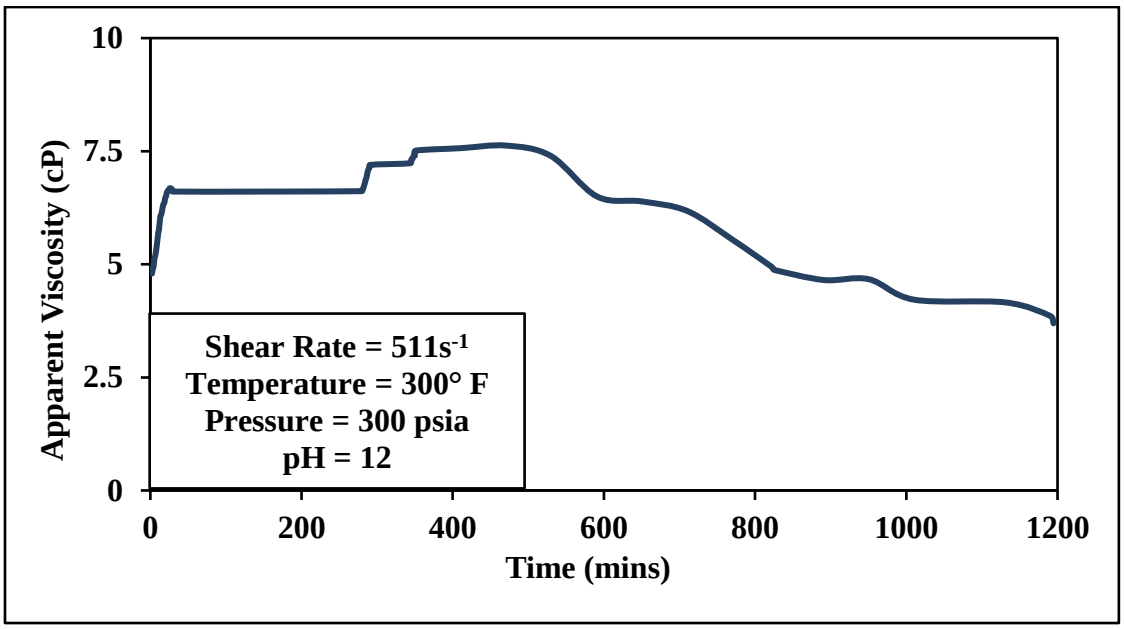

Figure 4.29: Viscosity measurements of 5 wt.% GLDA with 20 pptg of AMPS

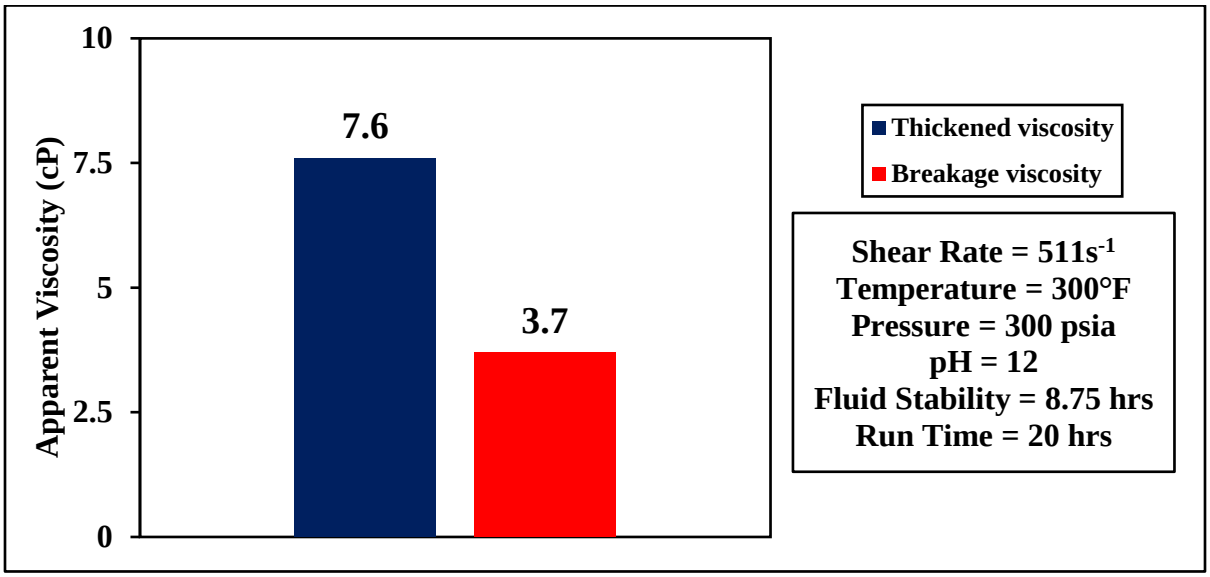

Figure 4.30: Stability Profile of 5 wt.% GLDA with 45 pptg of AMPS

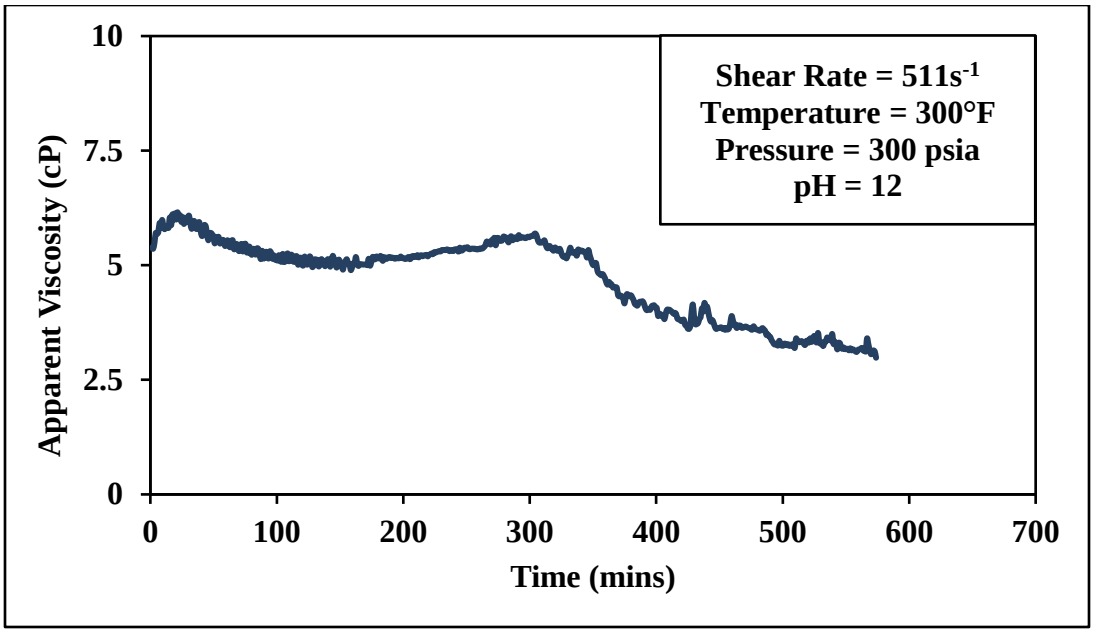

Figure 4.31: Viscosity measurements of 10 wt.% GLDA with 45 pptg of AMPS

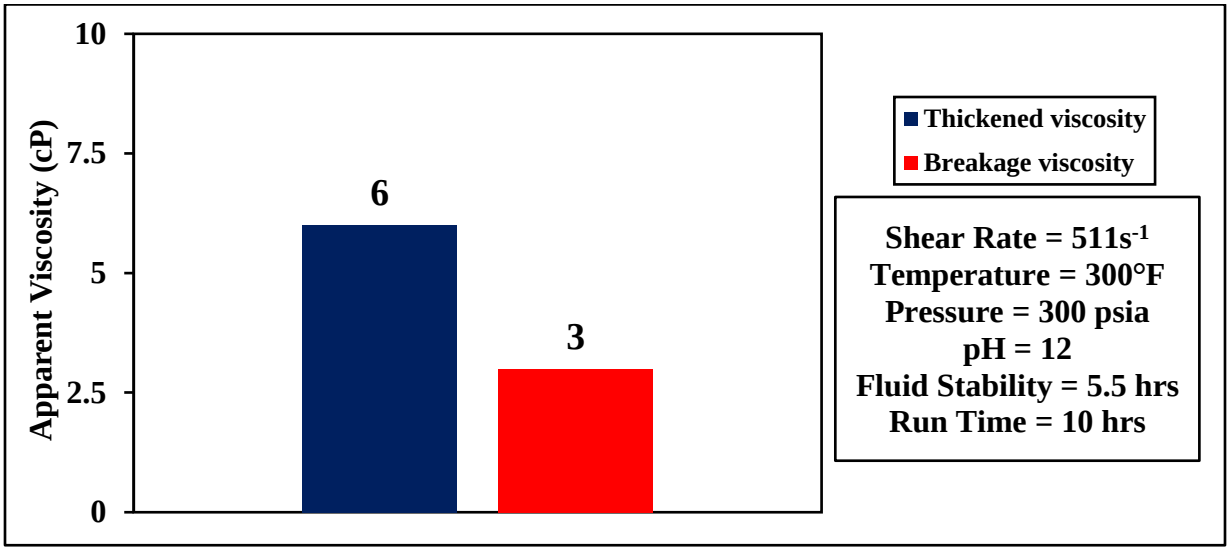

Figure 4.32: Stability profile of 10 wt.% GLDA with 45 pptg of AMPS

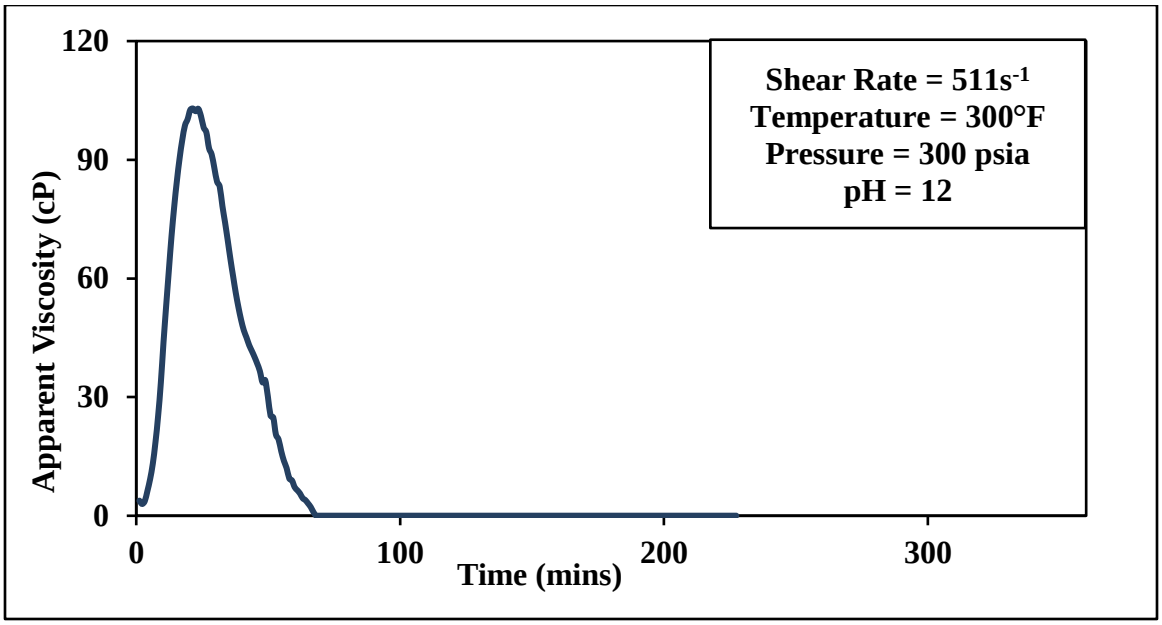

Figure 4.33: Viscosity measurements of 20 wt.% GLDA with 45 pptg of AMPS

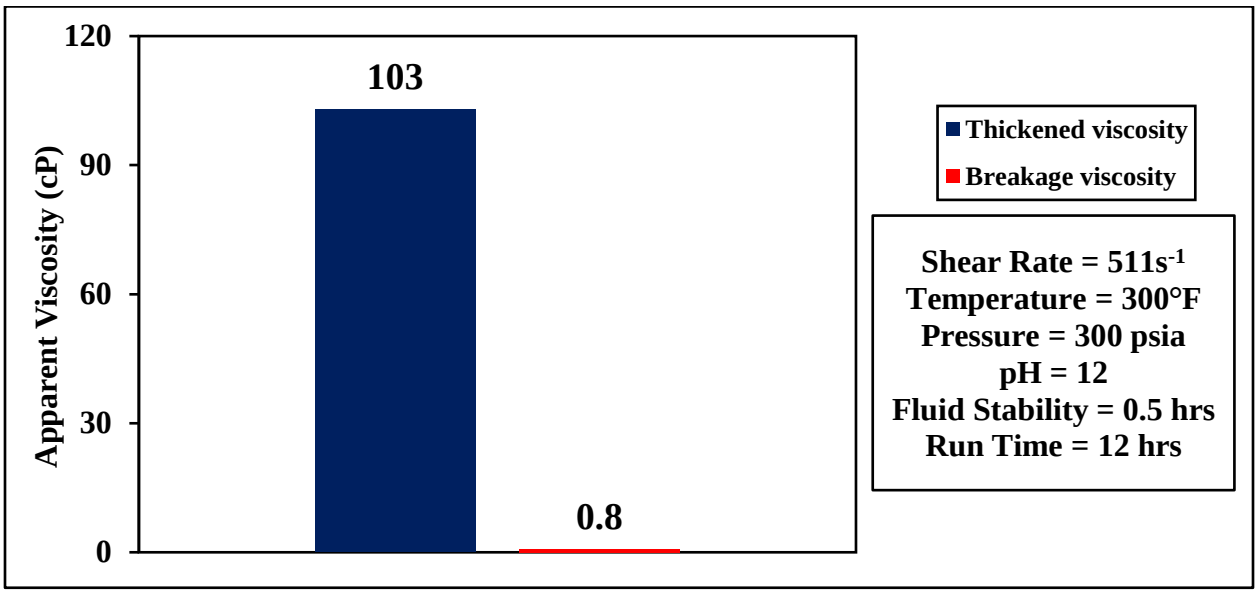

Figure 4.34: Stability profile for 20 wt.% GLDA with 45 pptg of AMPS

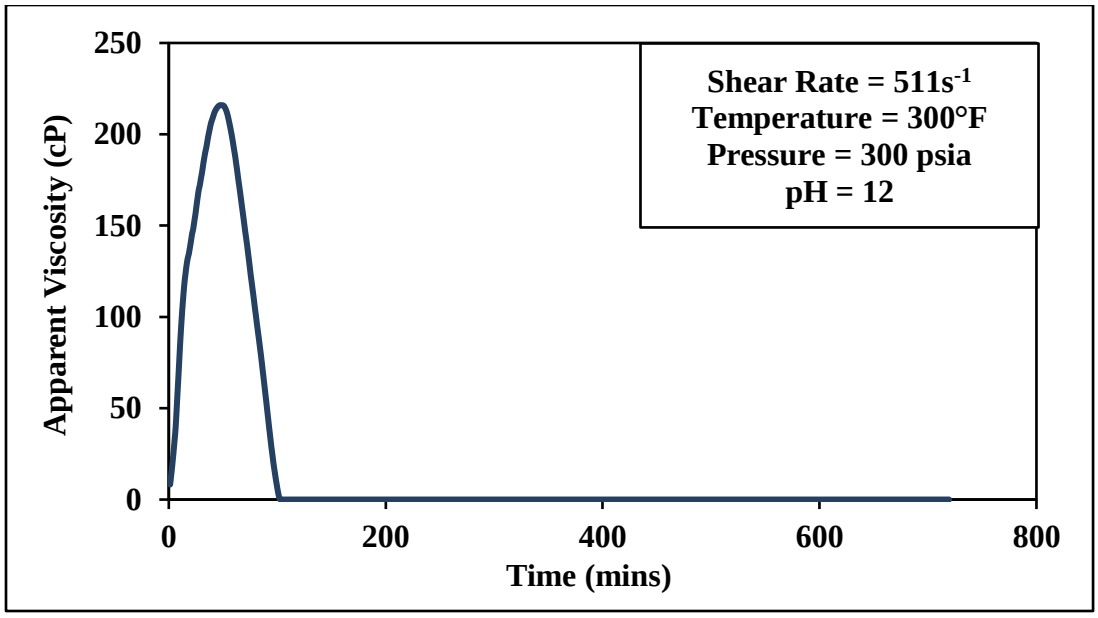

Figure 4.35: Viscosity measurements of 30 wt.% GLDA with 45 pptg of AMPS

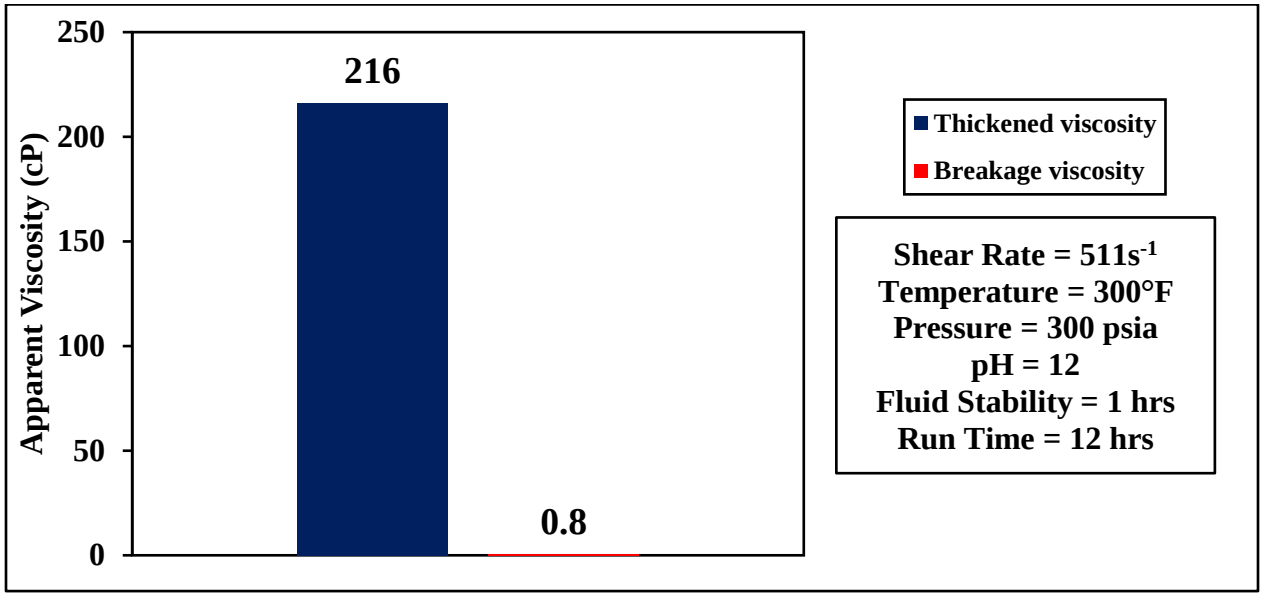

Figure 4.36: Stability profile of 30 wt.% GLDA with 45 pptg of AMPS

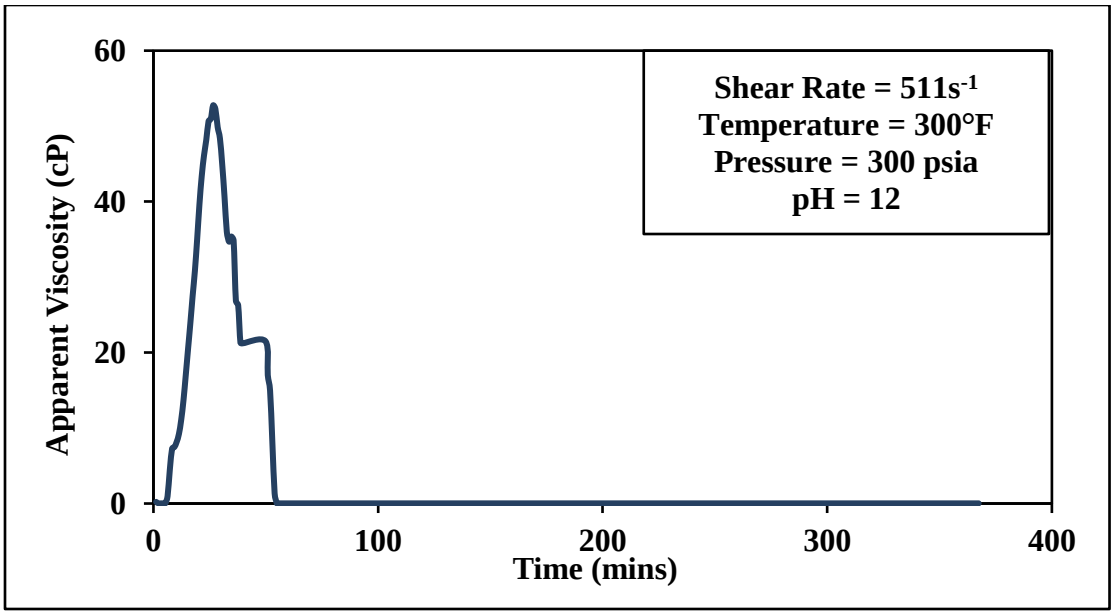

Figure 4.37: Viscosity measurements of 40 wt.% GLDA with 45 pptg of AMPS

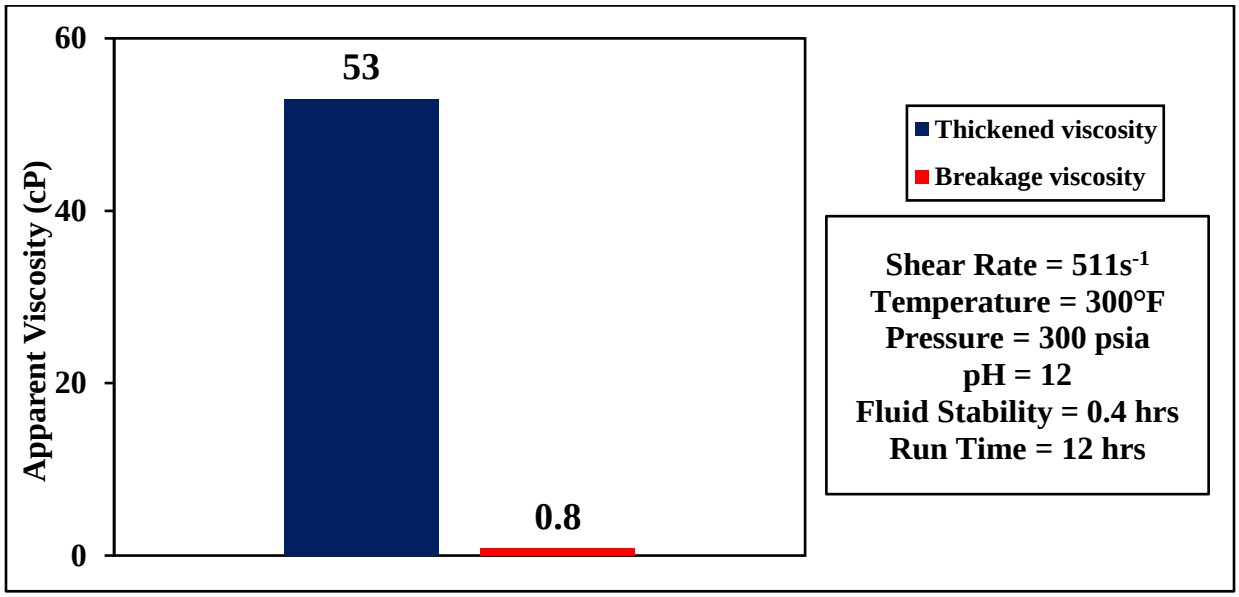

Figure 4.38: Stability profile of 40 wt.% GLDA with 45 pptg of AMPS

4.2.6 The effect of Shear rate on the fracturing fluid behavior

20 wt.% of GLDA and 20 pptg of AMPS were mixed and the apparent viscosity was measured versus mixing time, the pH of the mixture was fixed at pH 12 and temperature of 200°F. The experiment was conducted with varying shear rates (at $100s^{-1}$ & $511s^{-1}$).

As shown in Figure (4.39), increasing the shear rate will reduce the stability of the fluid mixture, which indicates that high shearing will break the polymer chains faster combined with the effect of GLDA as a breaker at high temperatures.

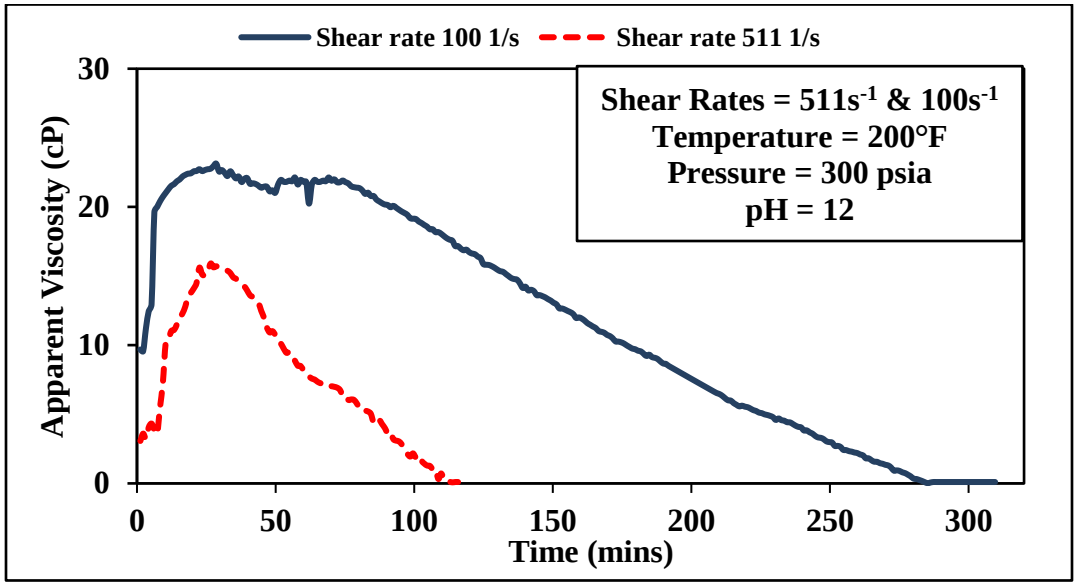

Figure 4.39: Viscosity measurements of 20 wt.% GLDA with 20 pptg of AMPS in different shear rates

Figure (4.40) represents the summary of the GLDA concentration study, it is shown that the optimum GLDA concentration that yields the highest viscosity is from 20 wt.% to 30 wt.% when mixed with 45 pptg of AMPS diluted in fresh water, this range of concentrations can be used to fracture unconventional sandstones.

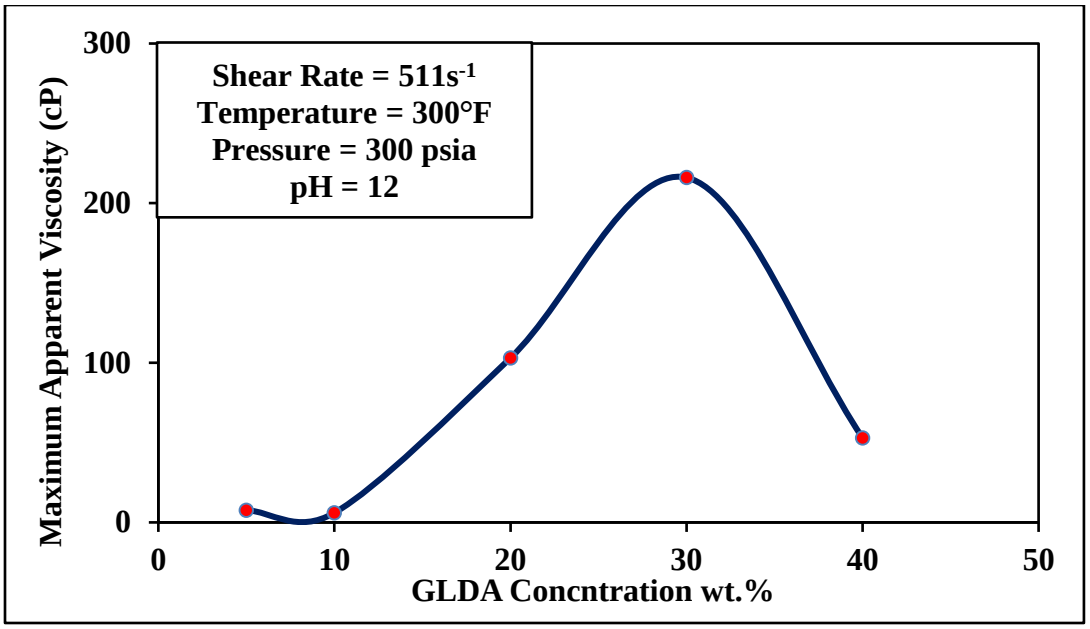

Figure 4.40: Concentration Optimization of GLDA with 45 pptg of AMPS

4.3 Development of the Fracturing Fluid Using Seawater

4.3.1 The effect of pH on the developed fluid behavior

20 wt.% of GLDA and 20 pptg of AMPS were mixed in seawater, the apparent viscosity was measured versus mixing time, the temperature was fixed at 200°F and the shear rate was $511s^{-1}$. The experiments were conducted at pH 4 and 7.

The results of this experiment showed that mixing GLDA with AMPS increased the viscosity from the basic viscosity of the polymer solution alone, and remained constant throughout the experiment, however at pH 7 the increase in the viscosity was greater than at pH 7 at the same conditions and at pH 12 the viscosity was even higher than both pH 4 and 7 which indicates that the viscosity increases with the increase of pH when using AMPS. However, increasing the pH of GLDA increased the stability of the solution and gave better thickened viscosity, compared to the results of the same conditions but using

DI-water, the breakage behavior noticed here is due to the addition of the seawater minerals to the solution which shrinks the polymer chains which drops the viscosity as it is noticed here. The results of the experiments are shown in Figure (4.41).

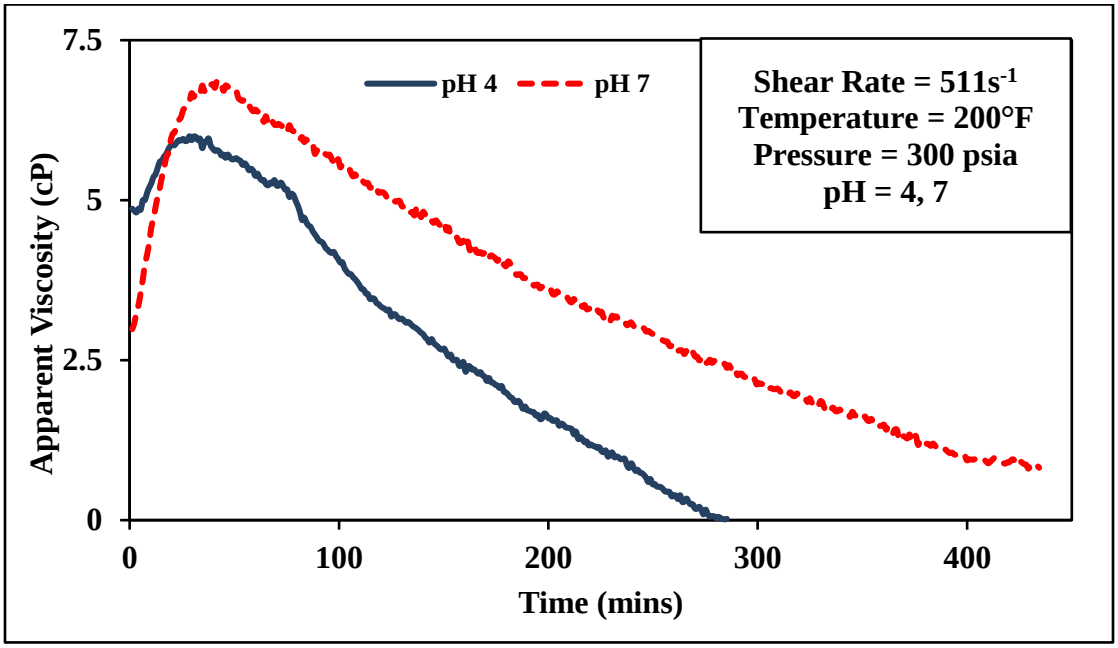

Figure 4.41: Viscosity measurements of 20 wt.% GLDA with 20 pptg AMPS at different pH values

4.3.2 The effect of Polymer concentration on the fracturing fluid behavior (Diluted in DI-water)

20 wt.% of GLDA was mixed with 20 and 70 pptg of AMPS in seawater, the apparent viscosity was measured against mixing time, the temperature was fixed at 200°F and the shear rate was $511s^{-1}$.

As shown in Figure (4.42), increasing the concentration of the polymer increased the viscosity of the fluid and delayed the breakage of the fluid, however introducing seawater to the formulation of the fracturing fluid decreased the built viscosity below what was observed using DI-water.

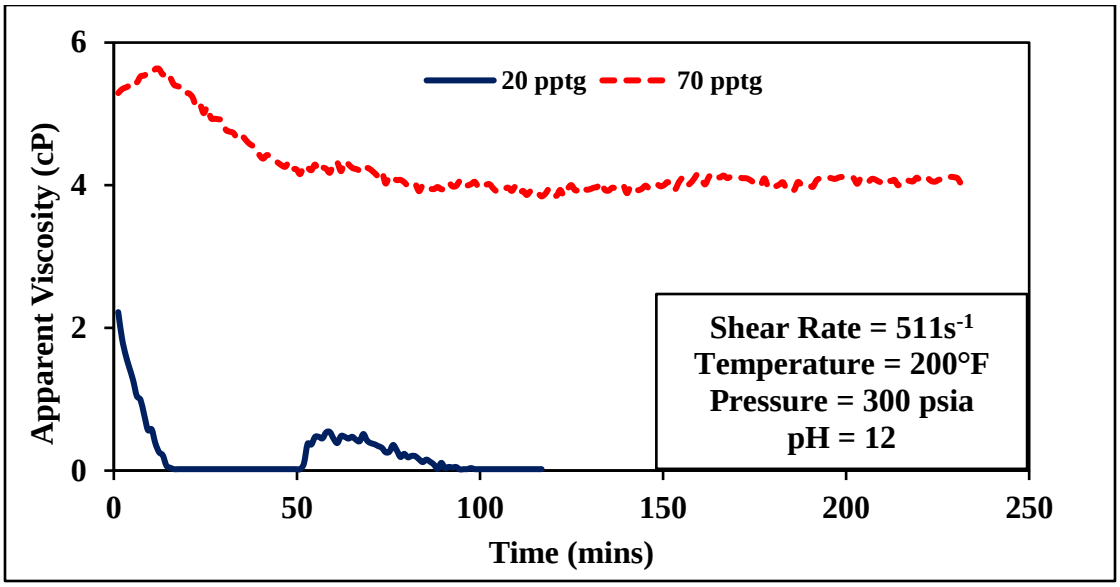

Figure 4.42: Viscosity measurements of 20 wt.% GLDA with AMPS at different concentrations

4.3.3 The effect of GLDA (Diluted in Seawater) concentration on the fracturing fluid behavior

Five experiments were conducted by mixing 45 pptg of AMPS with 5, 10, 20, 30, 40 wt.% of GLDA Diluted in Seawater, the apparent viscosity was measured with running time, the pH of the GLDA was fixed at 12, the shear rate at $511s^{-1}$, and the temperature at 300°F.

The results shown in Figures (4.43-4.52) indicates that increasing the GLDA concentration increases the viscosity of the solution, the optimum concentration when using seawater to dilute the polymer was found to between 10% to 15 wt.% of GLDA.

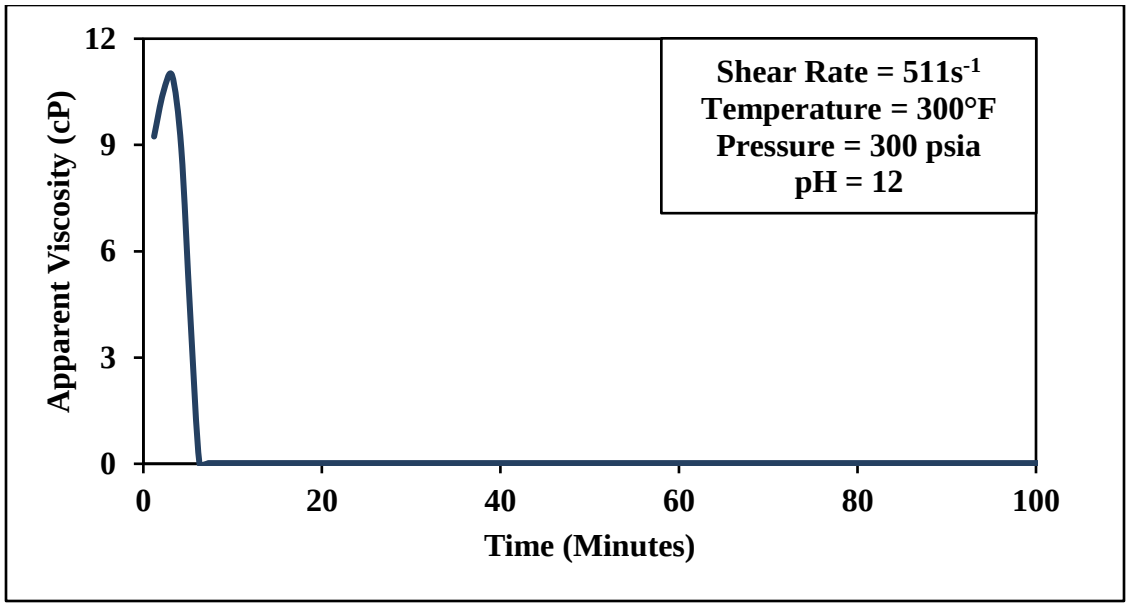

Figure 4.43: Viscosity measurements of 5 wt.% GLDA with 45 pptg of AMPS (Seawater)

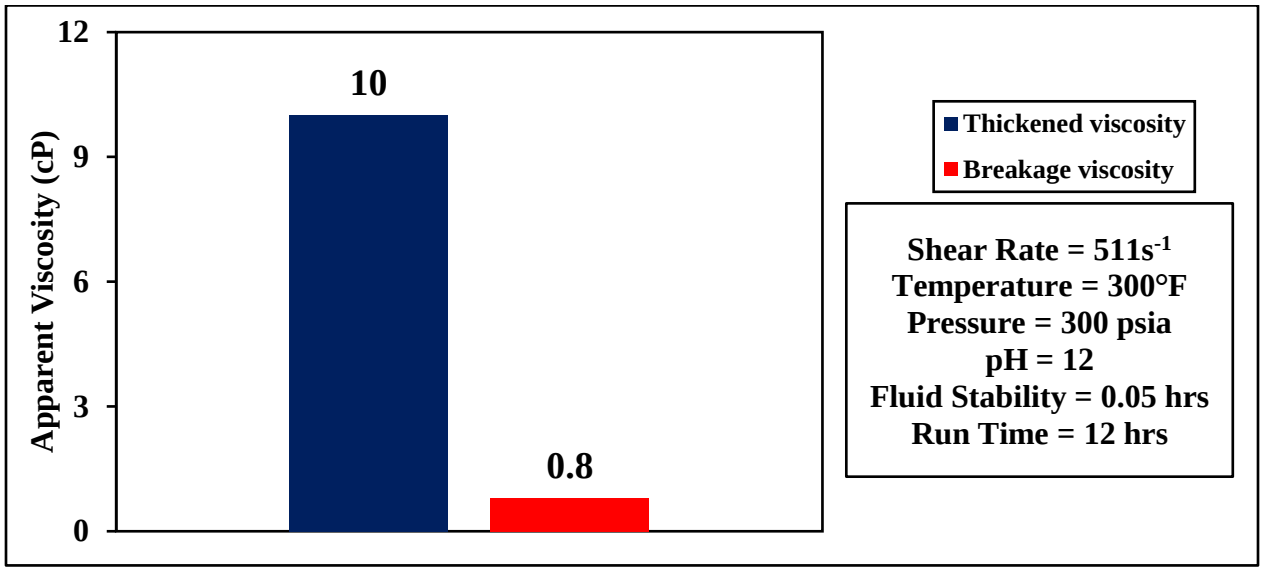

Figure 4.44: Stability profile of 5 wt.% GLDA with 45 pptg of AMPS (Seawater)

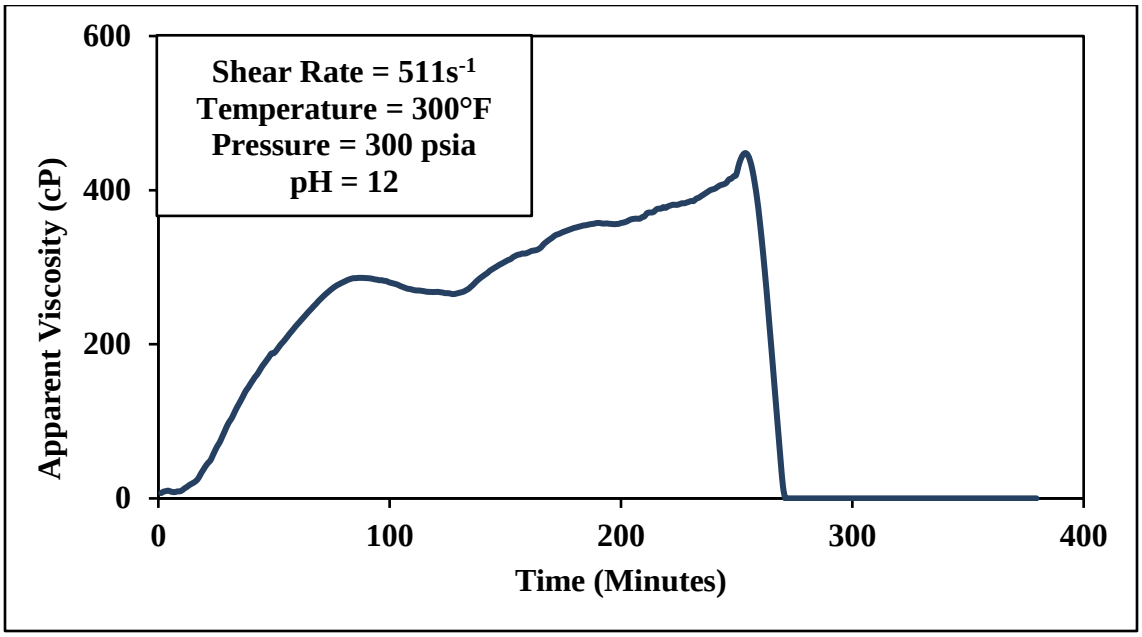

Figure 4.45: Viscosity measurements of 10 wt.% GLDA with 45 pptg of AMPS (Seawater)

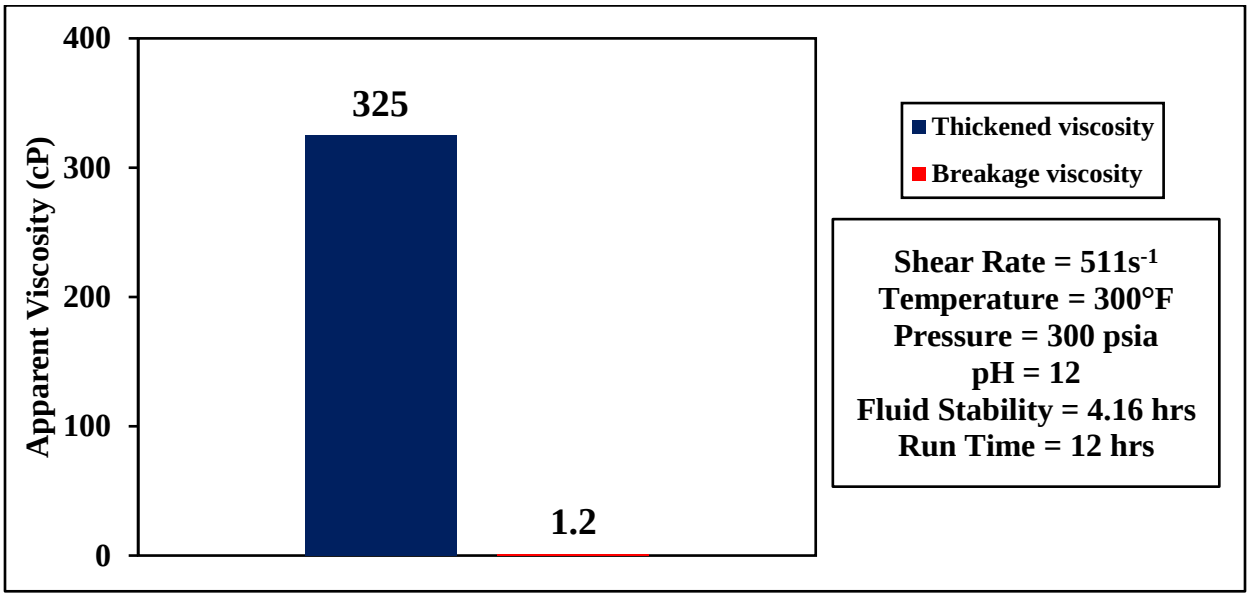

Figure 4.46: Stability profile of 10 wt.% GLDA with 45 pptg of AMPS (Seawater)

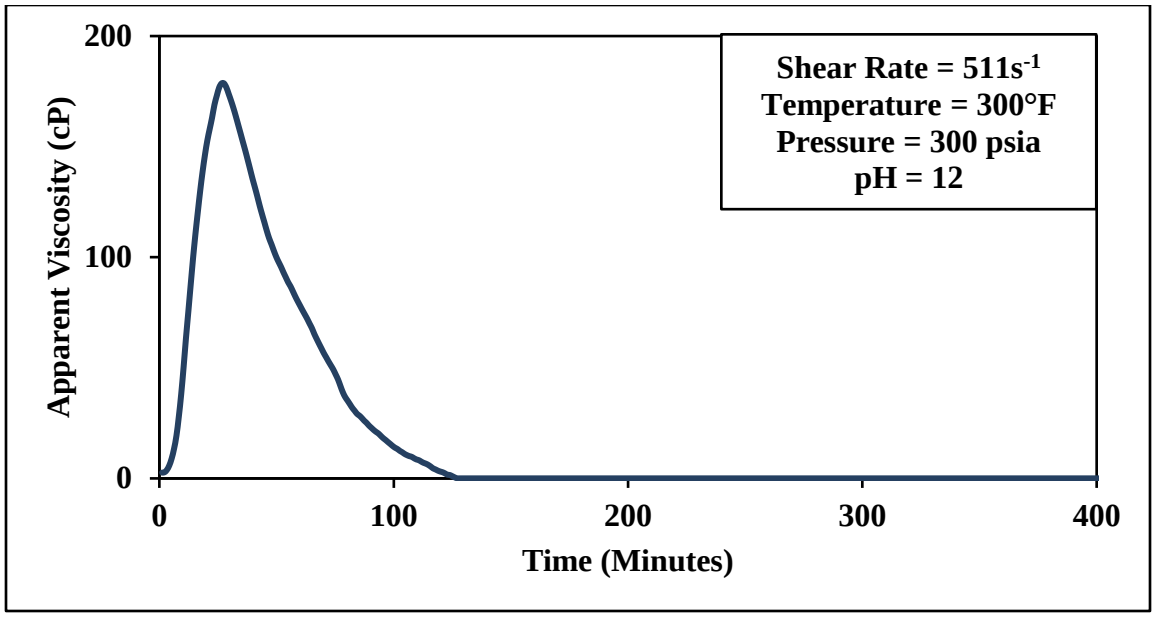

Figure 4.47: Viscosity measurements of 20 wt.% GLDA with 45 pptg of AMPS (Seawater)

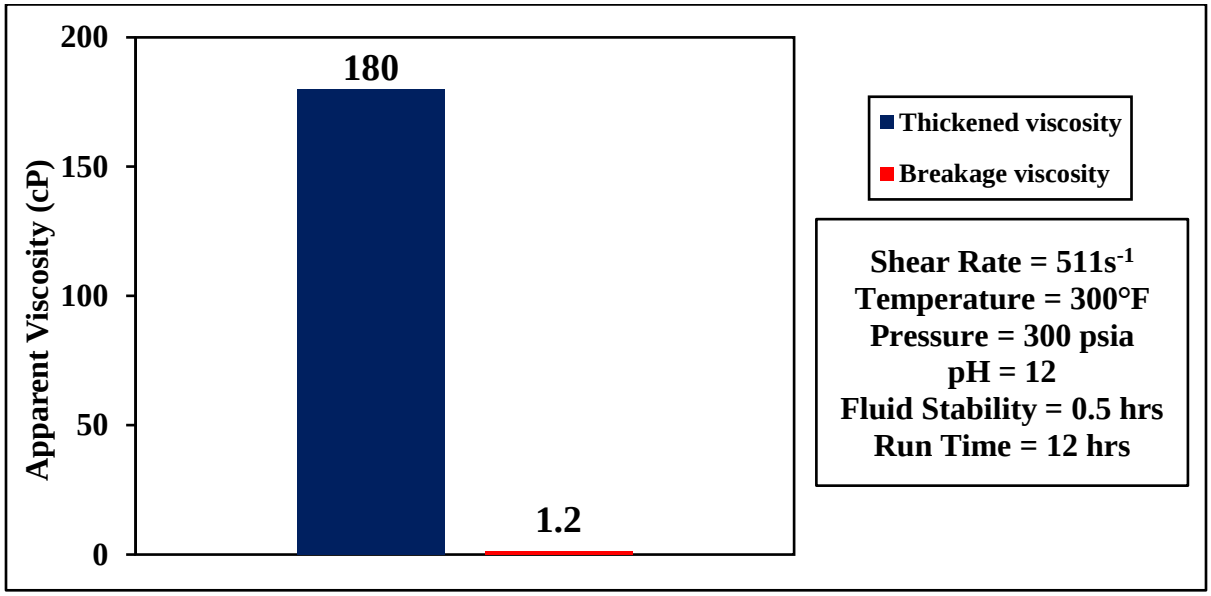

Figure 4.48: Stability profile of 20 wt.% GLDA with 45 pptg of AMPS (Seawater)

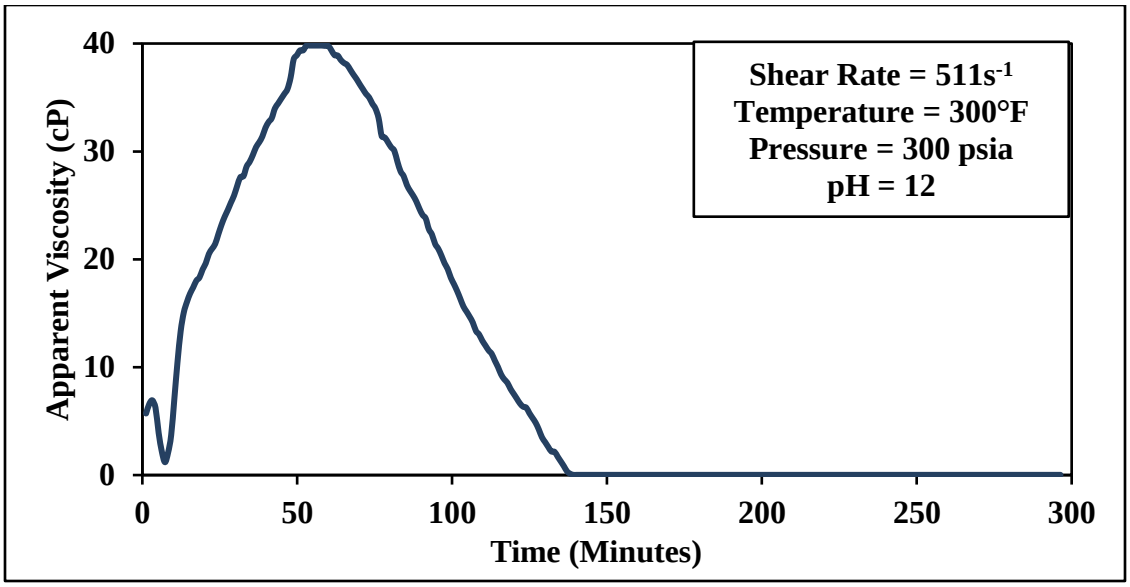

Figure 4.49: Viscosity measurements of 30 wt.% GLDA with 45 pptg of AMPS (Seawater)

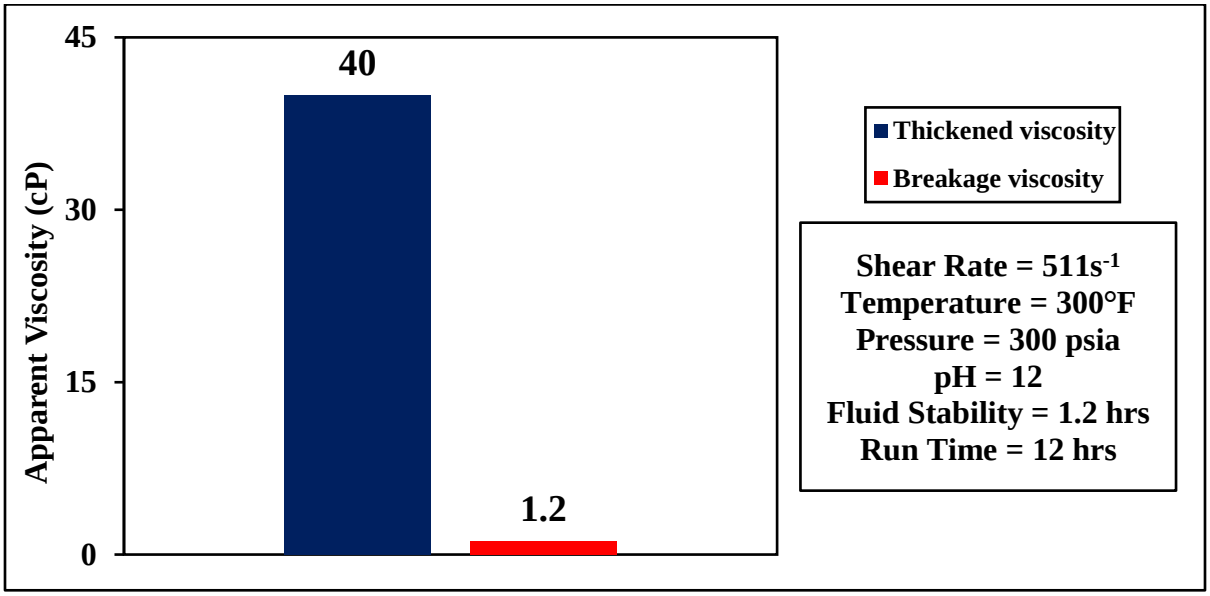

Figure 4.50: Stability profile of 30 wt.% GLDA with 45 pptg of AMPS (Seawater)

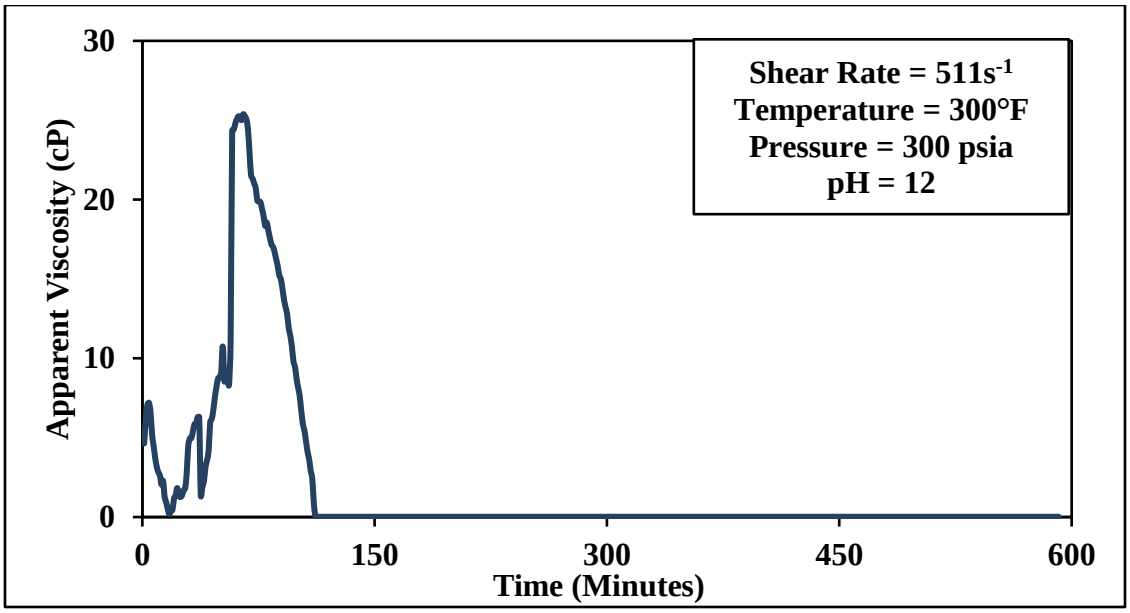

Figure 4.51: Viscosity measurements of 40 wt.% GLDA with 45 pptg of AMPS (Seawater)

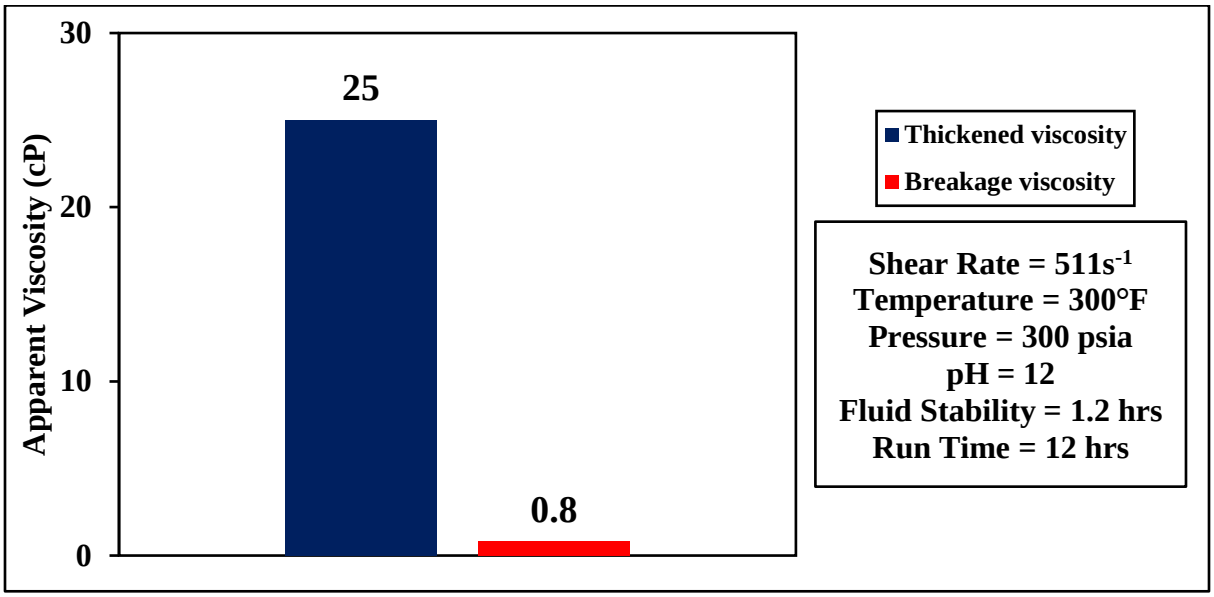

Figure 4.52: Stability profile of 40 wt.% GLDA with 45 pptg of AMPS (Seawater)

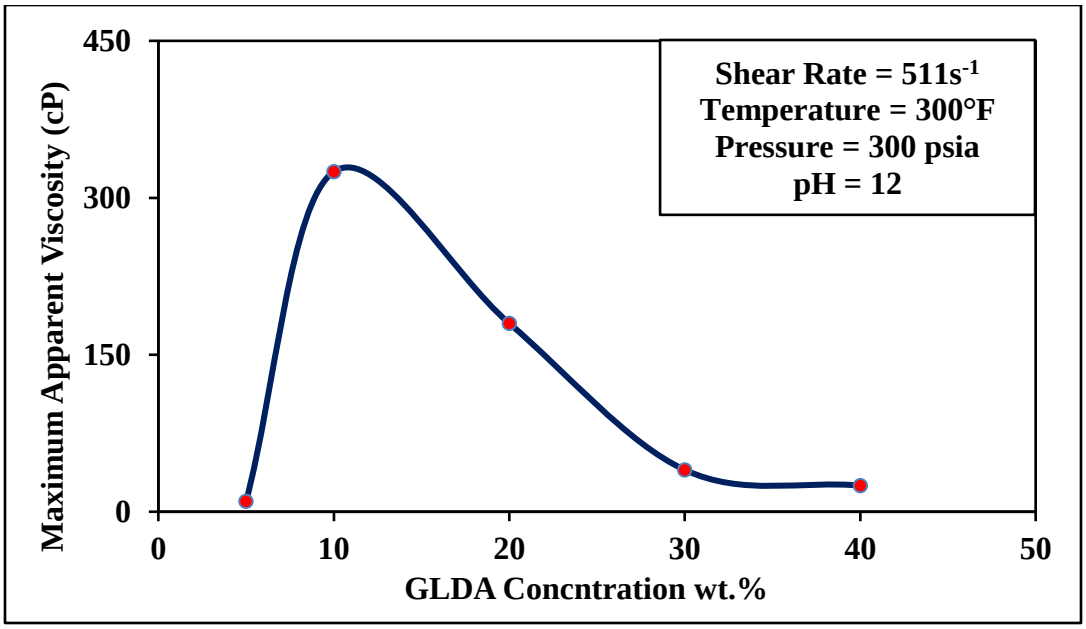

Figure 4.53: Concentration Optimization of GLDA with 45 pptg of AMPS (Seawater)

Figure (4.53) represents the summary of the GLDA concentration study, it is shown that the optimum GLDA concentration that yields the highest viscosity is from 10 wt.% to 20 wt.% when mixed with 45 pptg of AMPS diluted in Seawater, this range of concentrations can be used to fracture unconventional sandstones and can be used to replace slick water in fracturing operations.

4.4 Characterization and Evaluation of the Developed Fracturing Fluid on Sandstone core samples

Two sandstone core samples were cut and prepared for flooding using the continuous pumping setup shown in Figure (4.54). The core samples are first characterized in terms of porosity and permeability by weight measurements. The two core samples are shown in Figure (4.55).

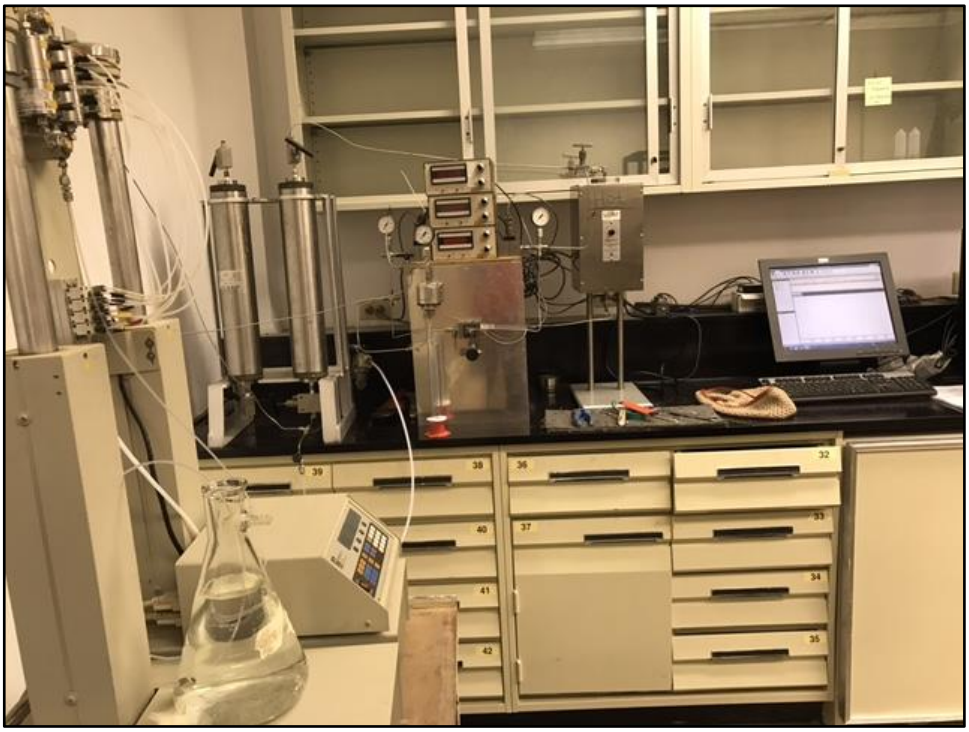

Figure 4.54: Continuous pumping setup

The core samples were weighted dry (after drying them up in the oven), and after saturation with 3 wt.% KCl. The brine permeabilities were measured using the continuous flow apparatus, core sample characteristics are shown in Table (4.2), and mineral composition of the core samples are shown in Table (4.3).

Table 4.2: Core Sample Characterization

Sample #	1	2
Type	Sandstone	Sandstone
Origin	Berea	Scioto
Diameter	2.5 inch	2.5 inch
Length	2 inch	2 inch
Dry Weight	349.56 g	354.96 g
Weight after Saturation	413.2 g	383.6 g
Water Weight	63.64 g	28.64 g
Pore Volume	63.64 g	28.64 cc
Bulk Volume	290 cc	240 cc
Porosity	22 %	12 %

Table 4.3: Mineral composition of the core samples

Minerals	Berea	Scioto
Quartz	86	70
Dolomite	1	--
Calcite	2	--
Feldspar	3	2
Kaolinite	5	Trace
Illite	1	18
Chlorite	2	4
Plagioclase	--	5

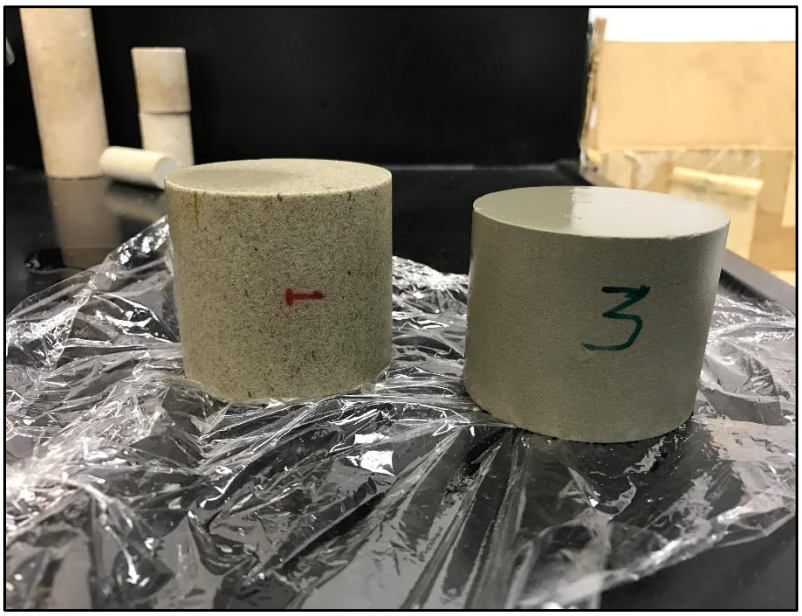

Figure 4.55: The core samples used in this study

4.4.1 Experiment using high permeability Berea Sandstone core sample

After saturating the core with 3 wt.% KCl, the core sample permeability has been measured using the set-up after the flow and pressure difference has been stabilized, Table (4.4) gives the result of the experiment. The permeability was calculated using Darcy's law:

$$k = 122.8\ \frac{q\ \mu\ L}{\Delta P\ D^2}$$

Table 4.4: Permeability measurements

Q (cc/min)	ΔP (psig)	k (mD)
20	5.3	148.3
10	2.6	151.14
5	1.3	151.14

The average permeability was found to be 151.2 mD. The fracturing fluid used in this core experiment consists of 20 wt.% of GLDA (at pH 12) mixed with 70 pptg of XC polymer in DI-water. The reason behind using high polymer concentration is the high permeability of the core sample which requires a thick fluid system. The viscosity of the developed fluid after thickening reached 200 cP.

The experiment was conducted in the conditions shown in Table (4.5):

Table 4.5: Experimental conditions and parameters

Conditions	Value
Injection rate (cc/min)	20
Inlet Pressure (Psig)	500
Back Pressure (Psig)	200
Temperature (°F)	300
Fracturing Fluid Volume (cc)	300

The experiment was conducted with a total running time of approximately 3 hours, the pressure profile of the experiment is shown in Figure (4.56 & 4.57).

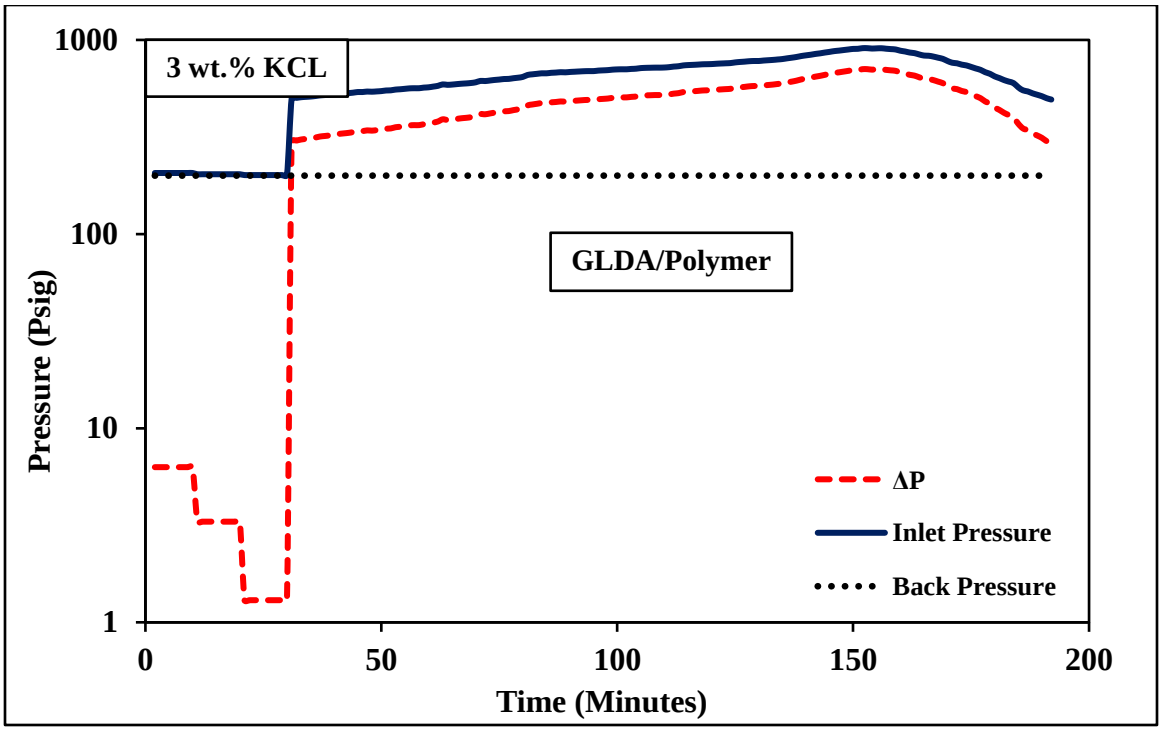

Figure 4.56: Core flooding experiment using Berea Sandstone core sample (pressure profile)

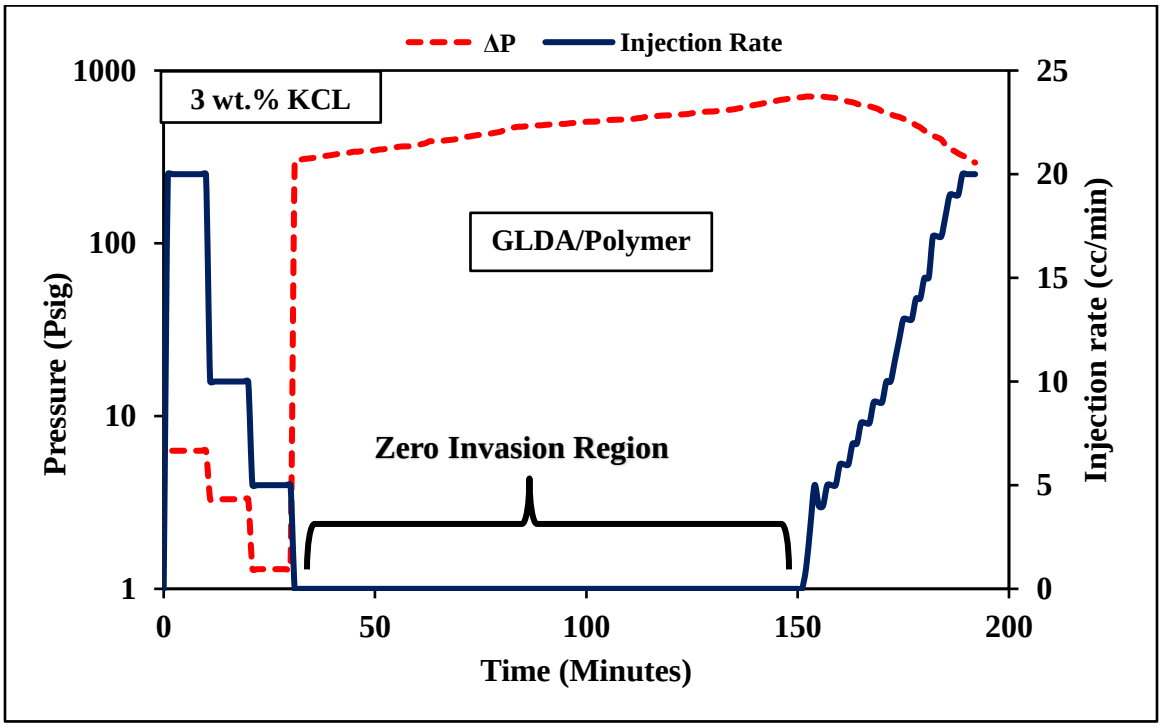

Figure 4.57: Core flooding experiment using Berea Sandstone core sample (pressure/Outlet flow profile)

It can be seen from the pressure profile that the fracturing fluid did not flow at the beginning of the experiment due to the high viscosity of the fluid which suggests that the thickening succeeded, the pressure difference required for this fluid to flow was 1048 psig using Darcy's law. Since the fluid was unable to flow through the core sample the pressure started to build up until the fluid started to gradually break and hence allowing the fracturing fluid to flow through the core. The pressure started dropping after approximately two hours from the start of the flooding.

The return permeability of the core sample was then measured by reversing the core and flowing it back with 3 wt.% KCl, the result of this experiment is shown in Table (4.6):

Table 4.6: Return Permeability measurements

Q (cc/min)	ΔP (psig)	k (mD)
20	6.3	124.75
10	3.3	119.08
5	1.3	140

The average return permeability was found to be 128 mD, and the regained permeability was found to be 85.2% of the original permeability. The sample after flooding is shown in Figure (4.58).

Figure 4.58: Berea Sandstone core sample after flooding

4.4.2 Experiment using low permeability Scioto Sandstone core sample

After saturating the core with 3 wt.% KCl, the core sample permeability was measured using the set-up after the flow and pressure difference has been stabilized, Table (4.7) gives the result of the experiment. The permeability was calculated using Darcy's law.

Table 4.7: Permeability measurements

Q (cc/min)	ΔP (psig)	k (mD)
20	205.3	3.83
10	100.3	3.92
5	52.3	3.76

The average permeability of the core has been found to be 3.837 mD. The fracturing fluid has been prepared using 20 wt.% of GLDA, 45 pptg of AMPS mixed in DI-water, the rheological profile of this fluid is shown in Figure (4.59).

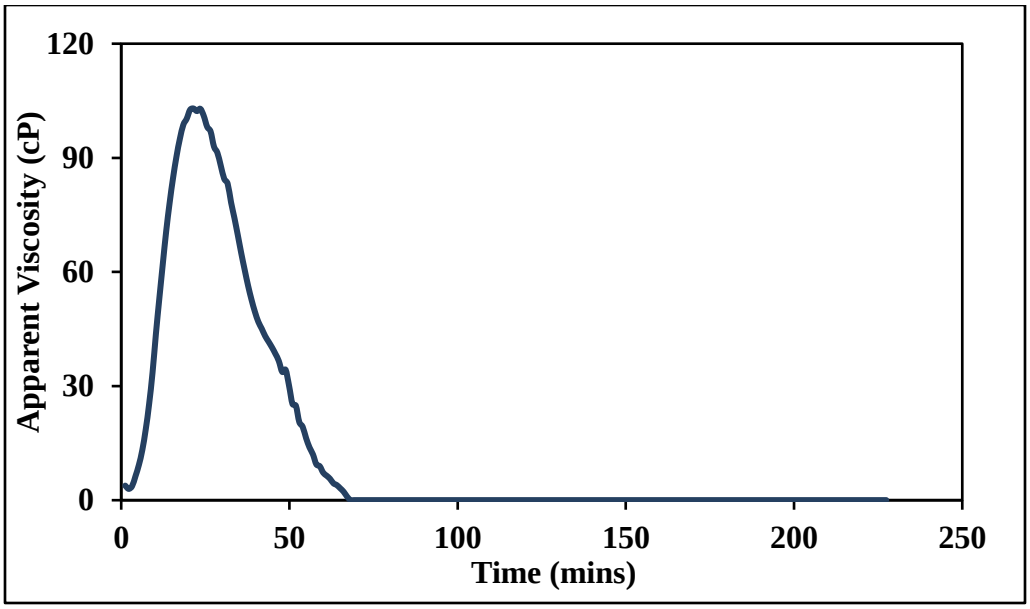

Figure 4.59: Rheological profile of the fracturing fluid used in Scioto Sandstone core sample

The core sample has been loaded up in the cell and to the setup to initiate the core flooding experiment. The experiment was conducted in the conditions shown in Table (4.8):

Table 4.8: Operational conditions and parameters

Conditions	Value
Injection rate (cc/min)	1
Inlet Pressure (Psig)	500
Back Pressure (Psig)	200
Temperature (°F)	300
Fracturing Fluid Volume (cc)	300

The experiment was conducted with a total running time of approximately 4 hours, the pressure profile of the experiment is shown in Figure (4.60 & 4.61).

It can be seen from the pressure profile that the fracturing fluid did not flow at the beginning of the experiment due to the high viscosity of the fluid which suggests that the thickening succeeded, the pressure difference required for this fluid to flow was 1025 psig using Darcy's law. Since the fluid was unable to flow through the core sample the pressure started to build up until the fluid started to gradually break and hence allowing the fracturing fluid to flow through the core. The pressure started dropping after two hours from the start of the flooding, this result is not with great conformance with the rheology and that is due to the effect of shear rate on reducing the stability of the fluid, whereas in this case the fluid is in static state, which prolonged the breakage of the fluid.

The return permeability of the core sample was then measured by reversing the core and flowing it back with 3 wt.% KCl, the result of this experiment is shown in Table (4.9):

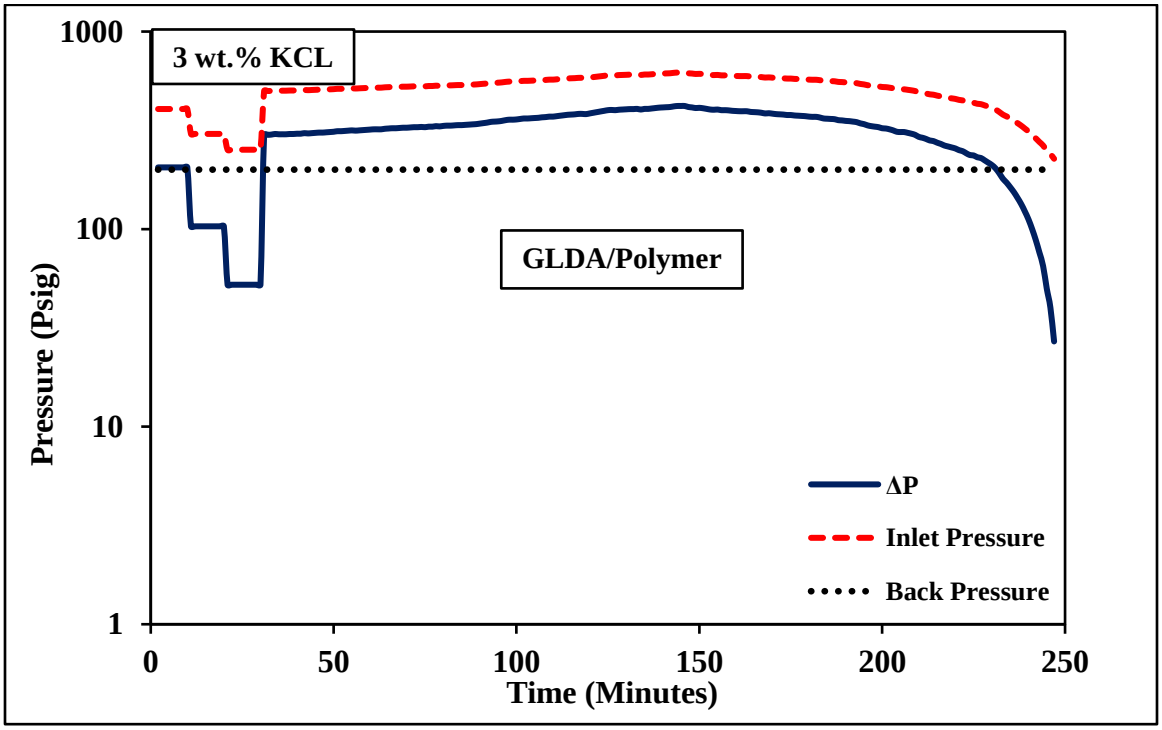

Figure 4.60: Core flooding experiment using Scioto Sandstone core sample (pressure profile)

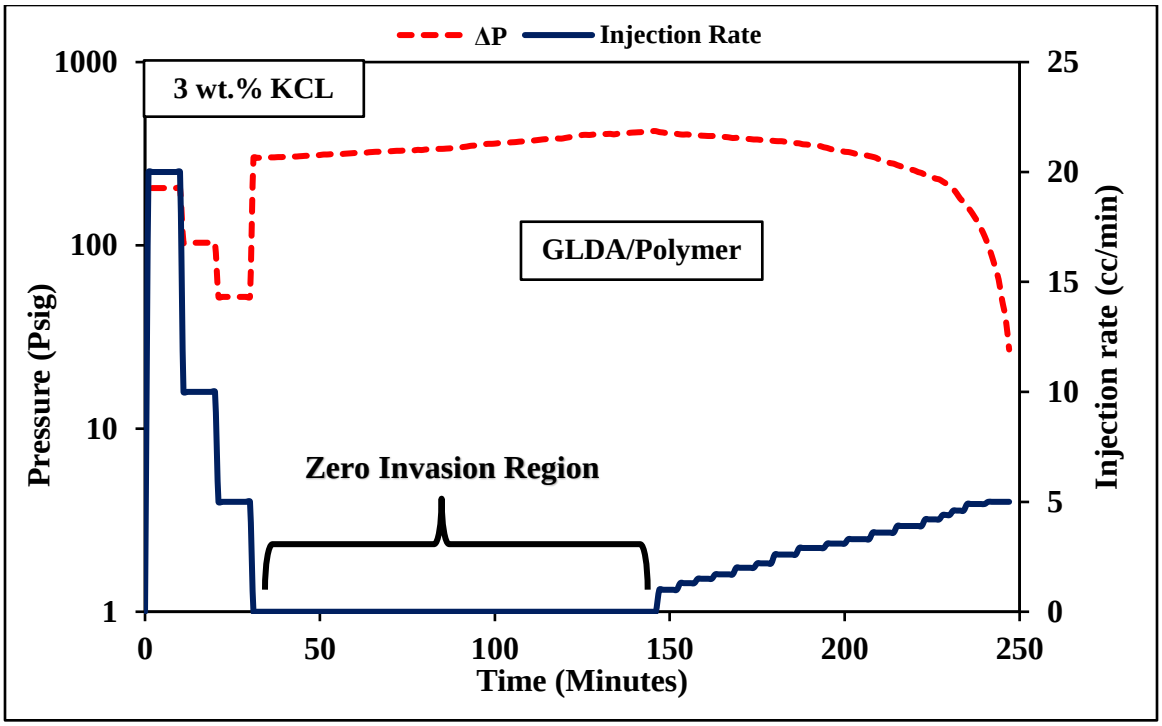

Figure 4.61: Core flooding experiment using Scioto Sandstone core sample (pressure/Outlet flow profile)

Table 4.9: Return permeability measurements

Q (cc/min)	ΔP (psig)	k (mD)
20	22.3	3.44
10	115.3	3.41
5	50.3	3.37

The average return permeability was found to be 3.4067 mD, and the regained permeability was found to be 88.8% of the original permeability. The sample after flooding is shown in Figure (4.62).

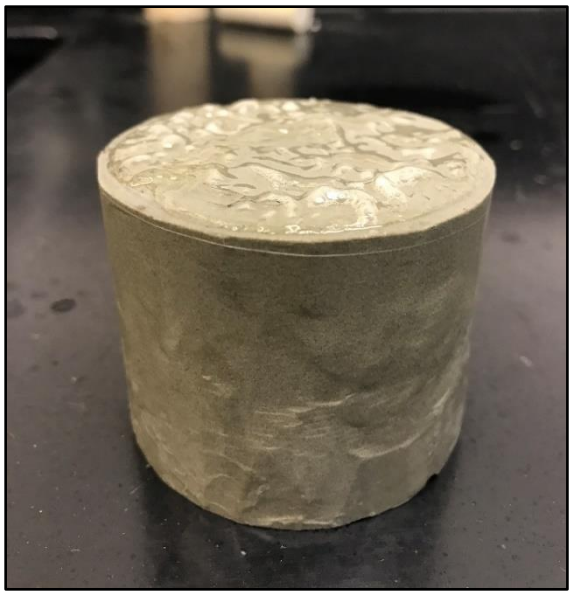

Figure 4.62: Scioto Sandstone core sample after flooding

Figure (4.63) shows the proposed field implementation of the developed fluid system on rheological profile obtained from the previous section.

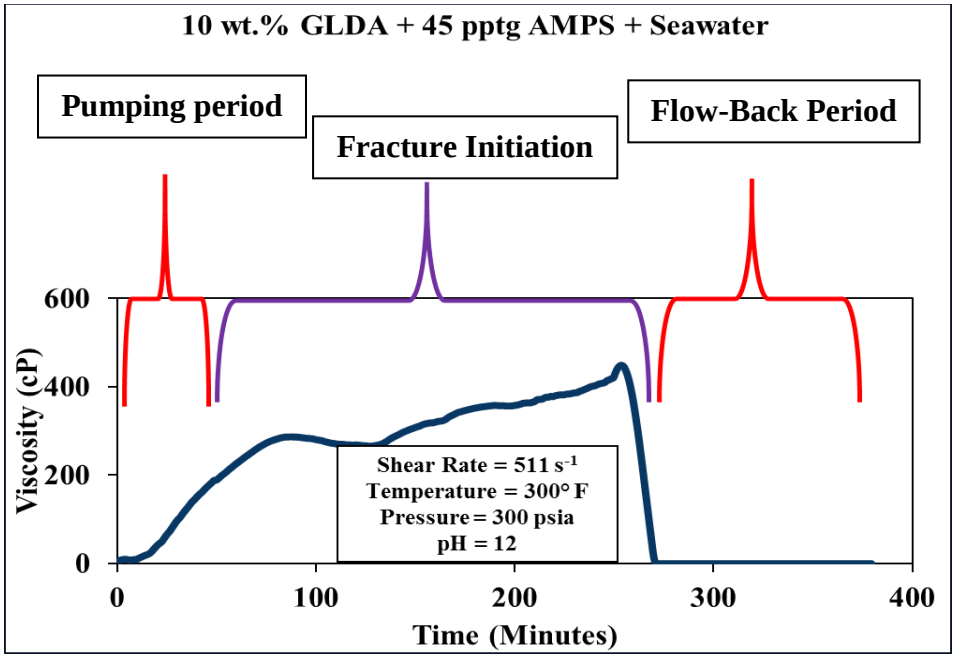

Figure 4.63: Field Implementation example

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this study a new simple, smart, environmentally-friendly fracturing fluid has been developed for fracturing tight sandstone formations, the fracturing fluid composes of Chelating Agents (GLDA, DTPA, and EDTA) and Polymers (AMPS, HPAM, TVP, HPG and XC have been evaluated) mixed in DI-water and Seawater. The new fluid acts as a cross-linker, breaker, biocide, clay stabilizer, friction reducer which replaces 8 additives that are essential in the formulation of a typical fracturing fluid.

The rheological properties were studied, the effect of temperature, pH, shear rate, GLDA concentration and polymer type and concentration were studied and investigated for the GLDA against AMPS polymer in terms of viscosity profiles and thickening-breaking profiles.

The study showed that the fluid will act as a thickening agent and breaker only at GLDA pH 12. And will only break at temperatures higher than the ambient temperature (77°F), while DTPA and EDTA thickens the fluid but did not break it. DTPA and EDTA were excluded from further testing due to this shortcoming.

The study showed that the optimum concentration of GLDA in the developed fluid formulation to be in the range from 20-30 wt.% when used with fresh water, and it will

yield a more stable fluid in high temperature (up to 300°F). the optimum concentration of GLDA when mixed with seawater was found to range from 5 wt.% to 10 wt.% and will yield a stable fluid in temperature of 300°F and shear rate of $511s^{-1}$.

The optimum polymer type and concentration depends on the application of which the fluid is intended to be used for.

Fourier Transform Infrared Spectroscopy Analysis was conducted to obtain the functioning groups that are responsible for the thickening and breaking of the developed fracturing fluid and to capture the chemical reactions that occur on the developed fluid. This study showed that the main groups responsible for the thickening and breaking effect are the Amide group (present in the polymer used) and the Carboxyl group (present in the GLDA).

Thermogravimetric Analysis was also conducted on the polymers under investigation and the effect of temperature on polymer degradation was studied. This study showed that the polymers screened in this research was resistive to high temperatures and no significant mass loss occurred.

Coreflooding experiments was conducted on a low and a high permeability sandstones core (Scioto & Berea) to prove the effectiveness of the developed fluid, by treating the core's surface as the fracture face and study the invasion of the fluid to the core, and the return permeability after the breakage to determine the reduction of permeability that occurred due to this flood. The core flooding of Scioto (low permeability core) yielded a return permeability of 89% and the fluid used composed of 20 wt.% of GLDA, 45 pptg of Co-polymer (AMPS) mixed in DI-water. The second core flooding experiment on Berea

sandstone yielded a return permeability of 85% and the fluid used to flood composed of 20 wt.% GLDA, 70 pptg of XC polymer mixed with DI-water. And the reason why the return permeability was low on this experiment is due to the high polymer concentration used which causes residual precipitation.

5.2 Recommendations

- For acid diversion stimulation applications, this study recommends using 20 wt.% of GLDA (at pH 12) mixed with 45 pptg of AMPS (Co-polymer) in fresh water. This formulation yields a good viscosity profile (up to 100 cP in $511s^{-1}$ shear rate) and stable for about one hour in high temperature formations (300°F).
- 5 wt.% of GLDA (pH 12) mixed with 45 pptg of AMPS (Co-polymer) mixed in seawater is a useful and great candidate fluid to replace slick water in shale and tight gas reservoirs applications, due to its good rheological profile (up to 135 cP at $511s^{-1}$ shear rate) and stable for about 3 hours in temperature of 300°F.
- 20 wt.% of GLDA (at pH 12) mixed with 70 pptg of XC polymer yielded a high return permeability (85%) when flooded in Berea sandstone (150 mD), and has a good and stable viscosity profile (up to 100 cP) in a temperature of 300°F. This formulation can be used to stimulate conventional sandstones efficiently.
- DTPA and EDTA thickens the fluid to a good value but a breaker must be used in order to reduce the viscosity of the thickened fluid which cannot break on its own like when using GLDA

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